VOL. XXII. SEPTEMBER, 1899. NO. 3.

AMERICAN

CHEMICAL JOURNAL

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON ALKYL MALONIC NITRILES AND THEIR DERIVATIVES.

BY JOHN C. HESSLER.

Monalkylated derivatives of malonic nitrile were prepared by P. Henry,[1] in 1889, by the distillation of the corresponding alkyl cyanacetamides with phosphorus pentoxide, but, except the determination of a few physical constants, no study of them has yet been made.

The experiments described in this paper were carried out at the suggestion and under the direction of Prof. Nef. Their object was the preparation and study of certain alkyl malonic nitriles, their salts, and other derivatives. The substances specifically studied were ethyl and benzyl malonic nitriles; the former had been prepared by Henry.[2]

The synthesis of alkyl malonic nitriles requires the preparation of alkyl cyanacetic ethers, which will now be described.

Preparation of Crude Ethylcyanacetic Ether.

The product obtained by Henry[3] from cyanacetic ether and ethyl iodide by the Conrad-Limpach method was found to be

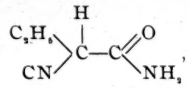
[1] Henry: Jahresber., 1889, 637; Belg. Acad. Bull. [3], **18**, 670.
[2] Henry: *Ibid.*
[3] Henry: *Ibid.*

a mixture of about 30 per cent. diethylcyanacetic ether and 70 per cent. monethylcyanacetic ether.

Fifty grams cyanacetic ether were mixed with 250 cc. absolute alcohol and treated with an alcoholic solution of 10.15 grams (1 atom) of sodium. 88 grams (1.25 molecules) of ethyl iodide were then added. The temperature rose to 40°, and within twenty minutes the solution was neutral to litmus. After the removal of the excess of alcohol and ethyl iodide by distillation water was added and the separated oil extracted with ether. The dried ether solution gave, on distillation, a substance boiling at 123°–124° at 50 mm., and at 206°–211° at ordinary pressure. The yield was 46 grams, or 74 per cent of the theoretical.

Thus prepared, crude ethylcyanacetic ether is a light and colorless oil, with an agreeable, ethereal odor. It is soluble in water to only a slight extent, but readily miscible with alcohol, benzene, and ether.

Sodium carbonate has no effect upon the substance, but aqueous sodium hydroxide dissolves it completely after several hours.

Ethylcyanacetamide,[1]  , was made by

treating 20 grams crude ethylcyanacetic ether with 17.2 grams (2 molecules) of 28 per cent ammonia. After twenty-four hours the amide which had crystallized out was filtered off, and the mother liquor distilled at reduced pressure (24 mm.). The water, which distilled at 30°–35°, carried with it a small amount of a light oil; a considerable amount of the oil followed at 110°–112°, and, finally, a product boiling at 180°–190°, which solidified in the condenser. This was ethylcyanacetamide (weight 4.5 grams). The total yield of amide from 20 grams oil was 8.5 grams.

The substance boiling at 110°–112° was separated from the water in the usual manner, and found to be pure diethylcyanacetic ether (see below). Its weight was 4.5 grams.

Ethylcyanacetamide is an odorless solid, soluble in water

[1] Cf. Henry: *Ibid.*

and in alcohol, almost insoluble in ligroin and in ether, and crystallizing from alcohol in colorless right prisms, which melt at 113°. The substance distils at reduced pressure (180°–190° at 24 mm.) without decomposition, and sublimes at temperatures near its melting-point. Toward sodium carbonate it is indifferent, but it is readily dissolved by aqueous sodium hydroxide, with evolution of ammonia. A portion was recrystallized twice from alcohol, and dried in an air-bath at 80° and *in vacuo* over sulphuric acid.

A nitrogen determination gave the following result:

0.0804 gram gave 19 cc. N_2 at 25° C. and 742 mm.

	Calculated for $C_5H_9NO_2$.	Found.
N	25.00	25.04

Diethylcyanacetic Ether,[1] $(C_2H_5)_2C(CN)C(=O)OC_2H_5$.—As stated above, crude ethyl cyanacetic ether made by the Conrad-Limpach method (Henry) was found to contain a considerable amount of a substance apparently unaffected by standing twenty-four hours with a concentrated solution of ammonia. The behavior of the crude oil toward sodium hydroxide, which dissolves the greater portion in a few minutes, and the remainder only after several hours, also establishes the presence of a neutral product. Its amount is found by treating 5 grams of the crude oil in ethereal solution with caustic soda. 1.5 grams remain unaffected by the alkali. This neutral product, which was obtained in large quantity in the conversion of crude ethylcyanacetic ether into the amide (see above), now boils at 215°–216°. It was redistilled and an analysis made, the resulting figures agreeing with those required by diethylcyanacetic ether.

I. 0.1434 gram substance gave 0.3317 gram CO_2, and 0.1159 gram H_2O.

II. 0.2139 gram substance gave 16.2 cc N_2 at 25° and 745.6 mm.

[1] Cf. Hesse: This JOURNAL, **18**, 746.

	Calculated for $C_9H_{15}NO_2$.	Found. I.	II.
C	63.90	63.10	....
H	8.87	8.98	....
N	8.28	....	8.33

The substance is a colorless liquid, of pleasant odor, boiling at 215°–216°, and readily miscible with organic solvents, but insoluble in water. It is indifferent to sodium carbonate, but slowly soluble in caustic soda. After some months' standing, even in the dark, it becomes yellow.

Diethylcyanacetic ether was treated with 28 per cent ammonia and allowed to stand two weeks. The product was recrystallized from alcohol and found to melt at 122°. Hesse[1] gives the melting-point of diethylcyanacetamide as 120°. Diethylcyanacetic ether was heated with concentrated hydrochloric acid in a sealed tube to 100° C. The contents of the tube were diluted with water and extracted with ether. The acid product was removed by shaking with sodium carbonate, acidifying with dilute sulphuric acid, and extracting with ether. Distillation of the latter left an oil, of acid odor, which solidified *in vacuo* over sulphuric acid. This substance melted at 54°–56°, and re-melted at 56°. Hesse[2] gives the melting-point of diethylcyanacetic acid as 57°.

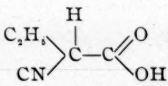
Persistent efforts were made to determine whether any cyanacetic ether was present in crude ethylcyanacetic ether, but not a trace of this substance could be found.

Henry[3] states that by several distillations of crude ethylcyanacetic ether he obtained a substance pure enough to be converted into amide, and that the vapor density and nitrogen determinations which he made gave figures that agreed with the theoretical. It is very unlikely, however, that he succeeded in effecting a complete separation, by fractional distillation, of diethylcyanacetic ether, boiling at 215°–216°, and ethylcyanacetic ether, boiling less than 10° lower. He states, further, that the ethylcyanacetic ether made by him was identical with that obtained by Haller[4] and by L. Henry[5] by the same method, and by Markownikow[6] from mercury and potassium cyanides and α-brombutyric ether.

[1] Cf. Hesse: *Ibid.* [2] Hesse: *Ibid.*
[3] Henry: Belg. Acad. Bull. [3], **18**, 670. [4] Haller: Compt. rend., **104**, 1627.
[5] L. Henry: *Ibid.*, **104**, 1619. [6] Markownikow: Ann. Chem. (Liebig), **182**, 330.

The mixed character of the product obtained by the action of cyanacetic ether and sodium alcoholate with ethyl iodide makes it probable that similar reactions carried out with other iodides always give mixtures of mono- and dialkylated cyanacetic ethers. For the same reason it seems unlikely that monalkylated malonic ethers have ever been obtained pure. The boiling-points of the substances are so close together that separation by fractional distillation is impossible, while the very slight differences in their composition prevent the detection in the monalkylated substances of small amounts of the dialkylated bodies.

Many similar cases have been observed and described, one of them by Nef[1] in his paper on acetoacetic ether derivatives.

Ethylcyanacetic Acid,  , was prepared by

treating 18 grams of crude ethylcyanacetic ether in ethereal solution with aqueous sodium hydroxide, which leaves diethylcyanacetic ether intact. The alkaline solution was treated with an excess of dilute sulphuric acid and extracted with ether. Distillation of the ether left a slightly colored oil of acid odor, distilling undecomposed at reduced pressure (160°–161° at 24 mm.). The yield was 6 grams.

A nitrogen determination gave the following result:

0.1152 gram substance 13 cc. N_2 at 26° C. and 747.3 mm.

	Calculated for $C_5H_7NO_2$.	Found.
N	12.39	12.39

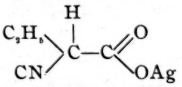
Ethylcyanacetic acid is a colorless, hygroscopic liquid with a faint odor, soluble in alcohol and in ether, and very soluble in water. At reduced pressure it distils without decomposition, but it is decomposed at ordinary pressures into carbon dioxide and butyronitrile, as is shown by the following experiment:

Three and four-tenths grams of the acid were heated in a flask to 170° C., at which temperature the substance decomposed into carbon dioxide and an oil boiling at 120°–140°.

[1] Nef: *Ibid.*, **266**, 116–122.

Weight of oil, 2 grams. Redistilled, the oil boiled at 118°–120°, and had the characteristic odor and other properties of butyronitrile.

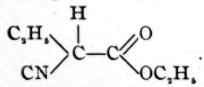
A brown liquid remained in the flask and solidified on cooling. This was soluble in sodium carbonate and precipitated by dilute sulphuric acid. Recrystallized from alcohol, the substance melted at 107°.5. It was undoubtedly slightly impure ethylmalonic acid (melting at 111°.5 when pure) formed by the saponification of some of the ethylcyanacetic acid.

Silver Salt of Ethylcyanacetic Acid,  . — This substance was made by neutralizing ethylcyanacetic acid with ammonia and adding concentrated silver nitrate. The precipitated silver salt was washed with cold water and dried *in vacuo*. A silver determination, made by ignition of the substance, gave the following result:

0.1990 gram substance gave 0.0970 gram silver.

	Calculated for $C_6H_4NO_2Ag$.	Found.
Ag	49.09	48.74

The silver salt is crystalline and, at first, perfectly white, but colors slowly in the light. The vapor that escapes when the substance is heated has the odor of butyronitrile.

Preparation of Pure Ethylcyanacetic Ether,  .—36 grams (about 3 molecules) of ethyl iodide were treated in a flask provided with a reversed condenser with 16.5 grams of the silver salt of ethylcyanacetic acid. Interaction took place on heating to 50°–55°, and 9.5 grams, *i. e.* 90 per cent of the theory, of ethylcyanacetic ether, boiling at 207°–209°, were obtained. To insure the removal of all ethyl iodide the product was heated with about 1 gram of silver ethylcyanacetate, and then redistilled.

An analysis gave the following results:

0.2018 gram substance gave 0.4430 gram CO_2, and 0.1428 gram H_2O.

	Calculated for $C_7H_{11}NO_2$.	Found.
C	59.57	59.86
H	7.80	7.86

Pure ethylcyanacetic ether is a colorless oil having a faint, sweet odor, noticeably different from that of the crude substance obtained by the Conrad-Limpach method. Its specific gravity at 22°.3 is 0.985.

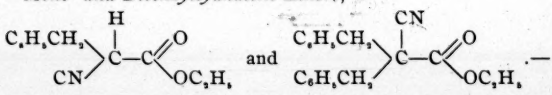
Action of Dry Sodium Cyanacetic Ether with Ethyl Iodide.

It seemed possible that the formation of the relatively large amount of diethylcyanacetic ether obtained in the Conrad-Limpach reaction was due to the presence of alcohol, and that, if dry sodium cyanacetic ether were treated with ethyl iodide, the amount of dialkylated substance might be considerably diminished. This proved to be the fact.

Dry sodium cyanacetic ether was prepared by adding sodium wire to a solution of cyanacetic ether in absolute ether. The yield of dry salt was regularly 95 per cent of the theory. 15 grams of sodium cyanacetic ether were heated in a sealed tube to 100° with 17.3 grams (1 molecule) of ethyl iodide and 10 cc. absolute ether. The contents of the tube were treated with water, and extracted with ether. Distillation of the ether left an oil boiling at 207°–209°, which had all the properties of crude ethylcyanacetic ether. Yield, 12 grams. Treatment with caustic soda showed that the product contained 1.5 grams, *i. e.* 12.5 per cent, of diethylcyanacetic ether. This method does not, therefore, avoid the formation of the dialkylated body, although it reduces its amount.

Action of Cyanacetic Ether with Alcoholic Sodium Ethylate and Benzyl Chloride.

Mono- and Dibenzylcyanacetic Ethers,



Judging from the results obtained in the preparation of ethylcyanacetic ether by the Conrad-Limpach method it seemed very likely that an attempt to prepare benzylcyanacetic ether

by the same method would likewise give a mixture of products.

Cassirer,[1] who was the first to carry out this experiment, states that he obtained from equimolecular quantities of cyanacetic ether, benzyl chloride, and sodium ethylate a heavy oil, which was saponified by alcoholic caustic potash to dibenzylcyanacetic acid. He seems to have overlooked entirely the small amount of monobenzylcyanacetic ether formed.

The experiment was carried out as follows: 20 grams cyanacetic ether, dissolved in absolute alcohol, were treated with an alcoholic solution of 4.07 grams (1 atom) of sodium, and with 22.4 grams (1 molecule) of benzyl chloride. The mixture was warmed on a water-bath for fifteen minutes, and found to be neutral to litmus. The alcohol having been distilled off, the residue was treated with water, extracted with ether, and the ethereal solution dried with calcium chloride. Distillation of the ether left a dark oil, which was distilled at reduced pressure (21 mm.), the fractions obtained boiling as follows: 1. below 78°; 2. 78°–128°; 3. 178°–238°. The first fraction consisted of alcohol and benzyl chloride, the second of benzyl chloride and a very small amount of cyanacetic ether, and the third of a colorless liquid boiling at 176°–183° at 21 mm., and a viscous, yellow liquid boiling at 234°–236° at the same pressure. These two substances were mono- and dibenzylcyanacetic ethers, respectively (see below). The yield of the former was only 2–3 grams, that of the latter 10–12 grams.

Owing to the fact that so small an amount of monobenzylcyanacetic ether was formed by the Conrad-Limpach method, it seemed better to treat dry sodium cyanacetic ether with benzyl chloride.

Action of Dry Sodium Cyanacetic Ether with Benzyl Chloride.

Twenty-seven grams of sodium cyanacetic ether were mixed in a flask with 25 grams (1 molecule) of benzyl chloride, and heated gently. Reaction began at 65°, and was complete at 80°. The product was treated with water, and the separated oil extracted with ether. The residue remain-

[1] Cassirer: Ber. d. chem. Ges., **25**, 3028.

ing after the evaporation of the ether was distilled at reduced pressure (20 mm.) in fractions boiling as follows:

Fraction.	Temperature.	Weight. Grams.
1	65°–76°	7.8
2	76°–120°	4.2
3	165°–210°	11.3
4	210°–233°	6.0

The first fraction consisted of benzyl chloride. The second was separated, by treatment with aqueous alkali, into benzyl chloride and an oil which crystallized on standing over sulphuric acid, melted at 66°–67°, and had the other properties of cyanacetic acid. Cyanacetic ether was, therefore, present in the second fraction.

The third portion was redistilled at reduced pressure (20 mm.) and found to boil chiefly at 176°–183°. It had all the properties of the corresponding fraction obtained by the Conrad-Limpach method. The oil boiling at 176°–183° was again distilled at 20 mm., and the portion boiling at 176° was analyzed, with the following results:

I. 0.1758 gram substance gave 0.4557 gram CO_2, and 0.1044 gram H_2O.

II. 0.2075 gram substance gave 13.1 cc. N_2 at 22° and 741.5 mm.

	Calculated for $C_{13}H_{13}NO_2$.	Found. I.	Found. II.
C	70.93	70.69	....
H	6.40	6.59	....
N	6.90	....	7.03

Three preparations, aggregating 42 grams of sodium cyanacetic ether, gave 16.4 grams of oil boiling at 165°–210° at 21 mm., from which 13.3 grams of almost pure benzylcyanacetic ether, boiling at 176°–185° at 21 mm., were obtained. Benzylcyanacetic ether is a colorless, limpid oil, having a faint aromatic odor. It is insoluble in water, but readily miscible with organic solvents. Toward sodium carbonate the substance is indifferent, but it reacts instantly with caustic soda, forming the sodium salt of benzylcyanacetic acid. If the alkaline solution is heated, ammonia is given off and the sodium salt of benzylmalonic acid is formed. With 28 per

cent ammonia, benzylcyanacetic ether reacts at once, forming benzylcyanacetamide.

The highest boiling fraction (4) obtained by heating dry sodium cyanacetic ether with benzyl chloride (see above) was redistilled at reduced pressure (20 mm.), and the portion boiling above 230° was treated in ethereal solution with aqueous sodium hydroxide, to remove any benzylcyanacetic ether which might be present. Distillation of the ether left a yellow oil boiling at 237° at 25 mm. Several attempts to solidify it proving unsuccessful, the substance was analyzed as a thick syrup, which had all the properties of the corresponding product obtained by the Conrad-Limpach method.

The analysis gave the following figures:

I. 0.4015 gram substance gave 1.1349 grams CO_2, and 0.2334 gram H_2O.

II. 0.1270 gram substance gave 0.3606 gram CO_2, and 0.0741 gram H_2O.

III. 0.5680 gram substance gave 24.6 cc. N_2 at 22° C. and 747 mm.

	Calculated for $C_{13}H_{15}NO_2$.	Found. I.	II.	III.
C	77.81	77.09	77.44	....
H	6.48	6.46	6.48	....
N	4.78	....	....	4.83

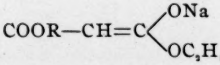
Dibenzylcyanacetic ether, obtained and analyzed as just described, in the form of a thick, viscous, yellow syrup, solidified after several weeks, forming large, colorless crystals, melting at 33°. The substance is insoluble in water and indifferent toward aqueous alkalies, but dissolves readily in alcohol and in ether.

Constitution of Sodium Cyanacetic Ether.

The work of Nef on acetoacetic ether, malonic ether, the nitroparaffins, etc., proves that the metallic salts formed by these compounds have the metal bound to oxygen. By analogy, sodium cyanacetic ether must have the constitution,

$$CN—CH=C\begin{matrix}ONa\\ OC_2H_5\end{matrix}, \qquad (I)$$

like that of sodium malonic ether,



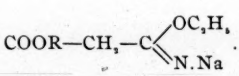
In connection with his experiments on cyanogen and isocyanogen compounds, Nef[1] was led to the consideration of another possible formula for the salt, namely,

$$COOC_2H_5—CH=C=N.Na. \qquad (II)$$

A salt of this constitution could indeed be formed by addition of sodium ethylate to the cyanogen group of the free cyanacetic ether,

$$COOR—CH_2—C \vdots N,$$

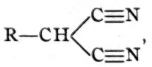
and subsequent loss of alcohol from the resulting addition-product,



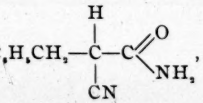
The formation of salts in the case of malonic nitrile,

$$CN—CH_2—C\equiv N,$$

and its monalkylated substitution-products,



does, in all probability, take place in this manner. The facts known at present, however, in regard to cyanacetic ether, point conclusively to formula (I) as representing the constitution of its sodium salt. Caustic alkalies and dilute acids convert the substance into cyanacetic acid, and ammonia forms with it cyanacetamide, in each of which substances the cyanogen group is unquestionably intact. This shows that the carbethoxy and not the cyanogen group is the point of attack when cyanacetic ether is treated with reagents. The same statement holds good in the case of its monalkylated substitution-products.

Benzylcyanacetamide,  , was prepared

[1] Nef: Ann. Chem. (Liebig), **287**, 281.

from pure benzylcyanacetic ether by treatment with a 28 per cent solution of ammonia. After twenty-four hours the crystalline mass was filtered off, washed with water, and recrystallized from alcohol.

An analysis resulted as follows :

I. 0.1980 gram substance gave 0.4990 gram CO_2, and 0.1036 gram H_2O.

II. 0.1007 gram substance gave 14.6 cc. N_2 at 22° C. and 744.2 mm.

	Calculated for $C_{10}H_{10}N_2O$.	Found. I.	Found. II.
C	68.96	68.74	....
H	5.74	5.81	....
N	16.09	....	16.16

For the preparation of benzyleyanacetamide in quantity it is much more economical to treat crude benzylcyanacetic ether, boiling at 165°–210° at 20 mm., directly with ammonia, and to free the product from a small amount of adhering dibenzylcyanacetic ether by recrystallization from alcohol. In this way it is possible to obtain about 15 grams of the amide from 50 grams of sodium cyanacetic ether.

Benzylcyanacetamide crystallizes from alcohol in large, colorless, right prisms melting at 130°, and from water in white needles. In ligroin and in ether it is only slightly soluble. Toward sodium carbonate the substance is indifferent, but sodium hydroxide dissolves it readily, even at the ordinary temperature, evolving ammonia, and forming the sodium salt of benzylcyanacetic acid (see below). At reduced pressure benzylcyanacetamide distils with little or no decomposition.

Action of Phosphorus Pentachloride upon Benzylcyanacetamide.

Benzylmalonic Nitrile, $C_6H_5CH_2CH(CN)_2$.—4.4 grams benzylcyanacetamide and 2.1 grams phosphorus pentachloride were mixed in a flask having a receiver, and the flask was exhausted to 20 mm., and heated. At 74° the mixture began to melt and to give off hydrochloric acid gas. The temperature was raised gradually until there was quiet fusion and the contents of the flask distilled over into the receiver. The yield of distillate, which solidified at once, was 3.2 grams, or 84 per

cent of the theory. The proportions of benzylcyanacetamide and of phosphorus pentachloride taken, correspond to 5 molecules of the former and 2 of the latter, similar proportions of cyanacetamide and of the pentachloride having been found by Hesse[1] to give the best yield of malonic nitrile. The substance was recrystallized from alcohol and dried over sulphuric acid.

An analysis gave the following results:

I. 0.1356 gram substance gave 0.3828 gram CO_2, and 0.0641 gram H_2O.

II. 0.1084 gram substance gave 17.5 cc. N_2 at 20°.5 C. and 739.1 mm.

	Calculated for $C_{10}H_8N_2$.	Found. I.	II.
C	76.92	76.99	....
H	5.13	5.25	....
N	17.95	....	17.99

Benzylmalonic nitrile is soluble in alcohol, ether, benzene, and acetic ether; sparingly soluble in ligroin (70°–80°) and in water. From alcohol it crystallizes in large, white rhombohedra melting at 91°; from ligroin and from water in long needles. The substance distils undecomposed at reduced pressure (174° C. at 23 mm.). Caustic soda dissolves the dry solid and extracts it from its ethereal solution. If the alkaline solution is poured at once into dilute acids, benzylmalonic nitrile is regenerated; if allowed to stand twenty-four hours at the ordinary temperature, ammonia is evolved, and the sodium salt of benzylcyanacetic acid is formed; if heated, more ammonia is given off, and the solution then contains the sodium salt of benzylmalonic acid.

Sodium Salt of Benzylmalonic Nitrile, $C_6H_5CH_2\underset{\displaystyle CN}{\underset{|}{C}}=C=N.Na$.

—This substance was prepared by treating 4 grams of benzylmalonic nitrile in absolute benzene solution with 0.6 gram (a slight excess) of sodium. Only slight action taking place at the ordinary temperature, the mixture was warmed and allowed to stand over night. The precipitated sodium salt was

[1] Hesse: This JOURNAL, 18, 726.

washed with benzene, and dried *in vacuo* over sulphuric acid. The yield was 3.5 grams, or 78 per cent of the theory.

A sodium determination resulted as follows :

0.2106 gram substance gave 0.0860 gram Na_2SO_4.

	Calculated for $C_{18}H_7N_2Na$.	Found.
Na	12.92	13.22

The salt is an almost white, amorphous powder, which absorbs moisture from the air, and then becomes dark and undergoes decomposition. Poured into dilute acids, the substance regenerates benzylmalonic nitrile in the form of a white, bulky precipitate. The salt was dissociated into benzylmalonic nitrile and sodium hydroxide on addition of water; on standing twenty-four hours most of the precipitated benzylmalonic nitrile redissolved, but a small amount remained undissolved after three days. This was accordingly filtered off, dried, and found to melt at 130°. When it was mixed with pure benzylcyanacetamide the melting-point of the latter was not lowered. The substance was, therefore, taken to be benzylcyanacetamide, formed by the addition of water to benzylmalonic nitrile. The filtrate contained the sodium salt of benzylcyanacetic acid, as was proved by acidifying with dilute sulphuric acid and extracting with ether. Evaporation of the ether left a substance melting at 101°–102° when purified, and identical in every respect with benzylcyanacetic acid (see below).

Behavior of Sodium Benzylmalonic Nitrile when Heated.— 4 grams of the sodium salt were heated in a flask, and began to decompose at 120° C. At higher temperatures the substance swelled up to a black mass several times its original bulk. The flask was accordingly exhausted to 20 mm. and carefully heated. As a result 0.7 gram of an oil, boiling at 120°–140° at the reduced pressure, was obtained. Hot water extracted from the black residue a substance which was precipitated as a slimy, brown solid on the addition of dilute nitric acid. This proved to be the so-called azulmic acid. A strong odor of prussic acid was noticed in the filtrate from the azulmic acid. Silver nitrate was therefore added, and a precipitate of silver cyanide ob-

tained. Its amount corresponded to 0.4-0.5 gram of sodium cyanide, or 36–45 per cent of the theory.

The oil boiling at 120°–140° was redistilled and analyzed with the following results:

I. 0.1222 gram substance gave 0.3724 gram CO_2, and 0.0763 gram H_2O.

II. 0.1401 gram substance gave 13.65 cc. N_2 at 16° C. and 743.5 mm.

	Calculated for C_9H_9N.	Found. I.	Found. II.
C	82.44	83.06	....
H	6.87	6.94	....
N	10.69	....	11.14

The figures obtained agree fairly well with those calculated for hydrocinnamic nitrile.[1] That the oil was actually this substance was proved by its conversion into hydrocinnamic acid when heated in a sealed tube with concentrated hydrochloric acid.

Silver Salt of Benzylmalonic Nitrile, $C_6H_5CH_2—\underset{\displaystyle CN}{\overset{\displaystyle |}{C}}=C=N.Ag$.—This substance was made by the method of Comstock and Kleeberg[2] and Tafel and Enoch.[3]

To a cold solution of 1.56 grams benzylmalonic nitrile in 150 cc. 66 per cent alcohol were added 1.7 grams (1 molecule) of silver nitrate in concentrated aqueous solution, and then, drop by drop, the calculated amount of half-normal caustic potash. A bulky, amorphous, white precipitate was formed, which was thoroughly washed by decantation with water, and dried *in vacuo* over sulphuric acid. The yield was 2.4 grams, or 90 per cent of theory.

A silver determination gave the following result:

0.1724 gram substance gave 0.0710 gram Ag.

	Calculated for $C_{10}H_7N_2Ag$.	Found.
Ag	41.06	41.18

The silver salt can be kept indefinitely *in vacuo* over sulphuric acid, but in the air, even when protected from the

[1] Cf. Hoffman: Ber. d. chem. Ges., **7**, 520.
[2] Comstock and Kleeberg: This JOURNAL, **12**, 498.
[3] Tafel and Enoch: Ber. d. chem. Ges., **23**, 104.

light, it soon becomes black, and emits an odor like that of hydrocinnamic nitrile. When the salt is treated with dilute nitric acid, benzylmalonic nitrile is regenerated. Methyl and ethyl iodides react instantly with the substance. Heated, it begins to decompose at 80°, and at higher temperatures becomes a hard, black mass. Ether then extracts some tarry material, and leaves a gray substance having the properties of silver cyanide. The dissociation of the silver salt of benzylmalonic nitrile into silver cyanide, and that of the sodium salt into sodium cyanide makes it very probable that their constitution is to be represented by the formula

$$C_6H_5CH_2C(CN)=C=N.M.$$

Assuming with Nef[1] that the double cyanides and fulminates and the double salts of isonitriles with cyanide of silver[2] have the constitution:

$$AgNC : CNK;$$
$$AgONC : CNOK;$$
$$RNC : CNAg,$$

it will be seen that the monalkylated malonic nitrile salts have an analogous constitution. Since Gautier has proved that potassium cyanide sets free the isonitrile from its double salt,

$$RNC : CNAg,$$

it was hoped that the silver salt of benzylmalonic nitrile might dissociate in an analogous manner. An experiment carried out with this object in view resulted as follows:

Silver benzylmalonic nitrile (3 grams) was added to aqueous potassium cyanide. The solution obtained was filtered from a white, insoluble substance, and treated with dilute nitric acid. This produced a precipitate of silver cyanide weighing 1.2 grams, or 80 per cent of the theory. The substance insoluble in the solution of potassium cyanide melted

[1] Ann. Chem. (Liebig), **298**, 313. This question is being investigated experimentally in this laboratory and will include a study of the ferro- and the ferricyanides. J. U. Nef.

[2] Gautier: Ann. chim. phys. [4], **17**, 203.

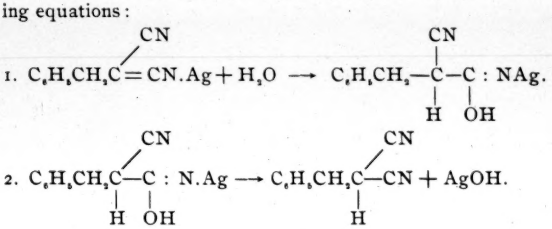
at 90° when recrystallized from ligroin, and had the other properties of benzylmalonic nitrile. Its weight was 1.1 grams, or 68 per cent of the theory. That this substance was actually benzylmalonic nitrile was proved by two nitrogen determinations, which gave the following results:

I. 0.1601 gram substance gave 25.4 cc. N_2 at 19°.5 C. and 738.5 mm.

II. 0.0984 gram substance gave 16 cc. N_2 at 23°.5 C. and 738.1 mm.

	Calculated for $C_{10}H_8N_2$.	Found. I.	II.
N	17.95	17.75	17.84

The action of potassium cyanide seems therefore to be a simple hydrolysis, and is probably represented by the following equations:



1. $C_6H_5CH_2C(CN)=CN.Ag + H_2O \longrightarrow C_6H_5CH_2-C(CN)(H)-C(OH):NAg.$

2. $C_6H_5CH_2C(CN)(H)-C(OH):N.Ag \longrightarrow C_6H_5CH_2C(CN)(H)-CN + AgOH.$

3. $AgOH + KNC \longrightarrow AgNC + KOH.$

Ethylmalonic Nitrile,[1] $C_2H_5-CH(CN)_2$.—5.6 grams of dry ethylcyanacetamide and 4.2 grams of phosphorus pentachloride were thoroughly mixed in a flask having a receiver. The apparatus was exhausted to 26 mm., and heat applied. The reaction took place at 80°, the mixture melted and became dark-colored, and hydrochloric acid gas came off in large quantities. The temperature was then raised very gradually to 100° or above, the end of the reaction being indicated by a violent frothing. This having ceased, the ethylmalonic nitrile formed distilled over at 90°–107°. The yield was 4 grams, or 85 per cent of the theory.

To free the product from any phosphorus oxychloride and ethylcyanacetamide which it might contain, it was shaken with water, dried, and redistilled.

[1] Cf. Henry: Jahresber., 1889, 637.

An analysis gave the following figures:

I. 0.1628 gram substance gave 0.3772 gram CO_2, and 0.0976 gram H_2O.

II. 0.1171 gram substance gave 0.2721 gram CO_2, and 0.0684 gram H_2O.

III. 0.1511 gram substance gave 39.2 cc. N_2 at 16° C. and 747.6 mm.

	Calculated for $C_5H_6N_2$.	Found. I.	II.	III.
C	63.83	63.20	63.38	....
H	6.38	6.65	6.49	....
N	29.79	....	....	29.85

Ethylmalonic nitrile is a light, colorless oil, only slightly soluble in water, but readily soluble in ether and in alcohol. Its odor is faint, and resembles that of acetamide. The substance boils at 90°–91° at 20 mm., and at 200° at the ordinary pressure (746 mm.). After a few weeks, even when kept in the dark, the oil becomes brown. It is indifferent to sodium carbonate, but dissolves readily in sodium hydroxide at the ordinary temperature with evolution of ammonia and formation of the sodium salt of ethylcyanacetic acid. If the alkaline solution is heated, more ammonia is evolved, and the sodium salt of ethylmalonic acid is formed.

Sodium Salt of Ethylmalonic Nitrile, $C_2H_5—\underset{\underset{CN}{|}}{C}=C=N.Na.$—

An ethereal solution of ethylmalonic nitrile does not react appreciably with metallic sodium even after two or three hours. If a drop of absolute alcohol is added, vigorous action begins, and an oil separates out which is insoluble in ether. A solution of ethylmalonic nitrile in pure benzene likewise reacts only very slightly with metallic sodium, even at the boiling-point of benzene. When the mixture was allowed to stand several days, however, a small amount of a slightly colored, amorphous powder was obtained. This was dried *in vacuo* over sulphuric acid, but decomposed so readily on exposure to the air that no further study of it was attempted.

Silver Salt of Ethylmalonic Nitrile,[1] $\begin{matrix} C_2H_5 \\ CN \end{matrix}\!\!>\!C=C=N.Ag.$—

[1] Cf. Henry: *Ibid.*

This substance was prepared in the same way as the silver salt of benzylmalonic nitrile, but greater precautions were taken to keep the temperature low.

Five grams ethylmalonic nitrile, dissolved in 50 per cent alcohol, were treated with an aqueous solution of 9 grams (1 molecule) of silver nitrate, and then with the calculated amount of a half-normal solution of caustic potash. During the addition of the alkali the mixture was kept cold by the introduction of pieces of ice, and was shaken vigorously. The amorphous, white precipitate of silver salt was washed by decantation with cold water, collected upon a filter, dried from five to ten minutes upon a clay plate, and then over concentrated sulphuric acid. Although the operations just described were carried out in a room at 2° C., the substance invariably decomposed after fifteen to twenty minutes. The decomposition was accompanied by a marked evolution of heat, and the bulky, white salt became black, pasty, and of small volume; at the same time water and an oil separated from the mass. The water held in solution a substance having an acid reaction and an odor like that of acetic or propionic acid. Ether and benzene extracted from the decomposed silver salt a small amount of a yellow oil, which was almost insoluble in water, but soluble in sodium carbonate and in sodium hydroxide. When these solutions were acidified the substance was apparently regenerated, but it could not be distilled without decomposition. Some of the oil was left standing several days, and deposited a white, crystalline solid melting at 134°. The amount of this substance was, however, so small that it was not examined further.

The black mass which had been treated with ether and with benzene was washed with hot alcohol and with water, and, finally, to free it from metallic silver, with dilute nitric acid. The residue thus obtained was a light gray, amorphous solid having the properties of silver cyanide. Heated, it was decomposed into silver and cyanogen, as is shown by the following results, which were obtained from independent preparations of silver ethylmalonic nitrile:

I. 0.3548 gram substance gave 0.2758 gram Ag.

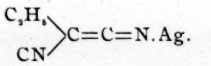
II. 0.0845 gram substance gave 0.0658 gram Ag.

III. 0.0989 gram substance gave 0.0775 gram Ag.

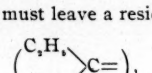
	Calculated for AgNC.	Found. I.	II.	III.
Ag	80.59	77.73	77.87	78.36

A small amount of tarry material, which adhered to the silver cyanide and escaped only upon ignition, was, no doubt, the cause of the low results.

In the case of the silver salt of ethylmalonic nitrile, as in that of the silver salt of benzylmalonic nitrile, all attempts to get both organic residues failed. Yet the spontaneous dissociation of these salts into silver cyanide, the formula of which has been determined by Nef[1] to be Ag—N=C, makes it extremely probable that in them the metal is bound to nitrogen. The formula of silver ethylmalonic nitrile is, therefore, written



Loss of silver cyanide must leave a residue,



capable, no doubt, of oxidation and of polymerization, thus giving rise to a complex mixture of substances.

Most persistent efforts were made in the instance described above to determine the nature of these products. The amount of material used was inadequate for this purpose, but the work done established unquestionably their complex character.

The only positive results obtained, therefore, show that salts of monalkylated malonic nitriles dissociate into metallic isocyanides, M—N=C. In the case of silver ethylmalonic nitrile this takes place spontaneously at 0°, with silver benzylmalonic nitrile at 80°, and with the corresponding sodium salt at 120°.

Action of Malonic Nitrile with Alcoholic Sodium Ethylate and Benzyl Chloride.

Dibenzylmalonic Nitrile $(C_6H_5CH_2)_2=C=(CN)_2$.—3 grams

[1] Nef: Ann. Chem. (Liebig), **287**, 265-359.

malonic nitrile (made by the method of Hesse[1] from cyanacetamide and phosphorus pentachloride) were dissolved in absolute alcohol, and treated with an alcoholic solution of 1.05 grams (1 atom) of sodium, and with 5.75 grams (1 molecule) of benzyl chloride. The temperature of the mixture rose to 40°, and common salt was precipitated. On cooling, long, white crystals of dibenzylmalonic nitrile (see below) were deposited. These were filtered off and washed with water to free them from sodium chloride. The alcoholic filtrate left, on distillation, a white, crystalline mass. This was treated with hot water, in which dibenzylmalonic nitrile is insoluble, and a small amount of monobenzylmalonic nitrile obtained. The total yield of product was 3.6 grams, fully 90 per cent of this amount being dibenzylmalonic nitrile.

An analysis of this substance gave the following results:

I. 0.1372 gram substance gave 0.4128 gram CO_2, and 0.0716 gram H_2O.

II. 0.1558 gram substance gave 16.4 cc. N_2 at 24° and 741.8 mm.

	Calculated for $C_{17}H_{14}N_2$.	Found. I.	Found. II.
C	82.93	82.07	....
H	5.69	5.79	....
N	11.38	....	11.58

Dibenzylmalonic nitrile is a white, crystalline solid melting at 131°. It dissolves in hot alcohol and in ether, is slightly soluble in hot ligroin, and insoluble in water. Toward aqueous alkalies, even when hot, it is entirely indifferent.

Action of Dry Sodium Malonic Nitrile with Benzyl Chloride.

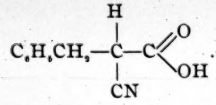
Dry sodium malonic nitrile, made according to the method of Schmidtmann,[2] was heated in a flask with the calculated amount of benzyl chloride with the expectation that a relatively larger amount of monobenzylmalonic nitrile than that produced by the Conrad-Limpach method might be formed. The reaction, accompanied by much charring, took place at 90°. The dark product was treated with boiling ligroin several times, and a white, crystalline substance obtained, which proved to be a mixture of mono- and dibenzylmalonic

[1] Hesse: This JOURNAL. **18**, 723.

[2] Schmidtmann: Ber. d. chem. Ges., **29**, 1171.

nitriles. Its amount was, however, very small. A similar result was obtained by heating dry sodium malonic nitrile with benzyl chloride and absolute ether in a sealed tube at 150° C.

Benzylcyanacetic Acid (*α-Cyan-β-phenylpropionic Acid*),



.—This substance was prepared by treating crude benzylcyanacetic ether in ethereal solution with aqueous sodium hydroxide and adding the alkaline solution to an excess of dilute sulphuric acid. The separated oil was extracted with ether, the ether dried, and distilled. The acid was thus obtained as a liquid, which solidified when cooled. It was recrystallized from benzene and an analysis made, with the following results:

I. 0.1140 gram substance gave 0.2856 gram CO_2, and 0.0543 gram H_2O.

II. 0.2068 gram substance gave 15 cc. N_2 at 20°.5 C. and 741.6 mm.

	Calculated for $C_{10}H_9NO_2$.	Found. I.	II.
C	68.59	68.33	....
H	5.14	5.29	....
N	8.00	....	8.11

Benzylcyanacetic acid is a white, crystalline solid, melting at 101°–102°, soluble in benzene, alcohol, and ether, and somewhat soluble in water. Hot caustic soda saponifies it, forming benzylmalonic acid. The substance cannot be distilled at ordinary pressure, since it decomposes into carbon dioxide and hydrocinnamic nitrile, as is shown by the following experiment:

Two and a half grams of the acid were heated in a flask to 170°–200°, carbon dioxide being evolved in large quantities. The residue in the flask was then dissolved in ether, the ethereal solution shaken with sodium carbonate, and dried with chloride of calcium. The ether left, on evaporation, an oil boiling at 253°; weight, 1 gram, or 53 per cent of the theory. That this substance was hydrocinnamic nitrile was

proved by heating it in a sealed tube with concentrated hydrochloric acid; hydrocinnamic acid, melting at 47°–48°, was thus formed.

Silver Salt of Benzylcyanacetic Acid, $C_6H_5CH_2CHCNCOOAg$. —This substance was prepared as follows: The acid was dissolved in ammonia, and the excess of the latter removed over sulphuric acid. The white ammonium salt, which had crystallized out, was redissolved in water and treated with a concentrated solution of silver nitrate. The silver salt was thus obtained as an amorphous, white precipitate, which became crystalline on standing. It was washed with water and dried over sulphuric acid. An analysis gave the following results:

I. 0.1270 gram substance gave 0.0480 gram Ag.

II. 0.0882 gram substance gave 0.0337 gram Ag.

	Calculated for $C_{10}H_8NO_2Ag$.	Found. I.	II.
Ag	38.29	37.80	38.21

The silver salt is precipitated, also, when concentrated silver nitrate is added directly to a concentrated aqueous solution of the acid. It is a heavy, white solid, which darkens slowly in the light. Heated to 140° it melts with decomposition, giving off a vapor having the odor of hydrocinnamic nitrile.

Benzoylbenzylmalonic Nitrile, $\begin{matrix} C_6H_5CH_2 \\ C_6H_5CO \end{matrix}\!\!>\!C=(CN)_2$.—2.7 grams of benzoyl chloride, dissolved in 20 cc. absolute ether, were treated in the cold with 3.4 grams (1 molecule) of sodium benzylmalonic nitrile. After twenty-four hours the benzoylbenzylmalonic nitrile was obtained as a crystalline mass. The substance was separated from the sodium chloride by means of boiling ether, recrystallized once from ether, and dried *in vacuo* over sulphuric acid. Yield 3 grams, or 60 per cent of the theory. A nitrogen determination gave the following result:

0.1579 gram substance gave 15.4 cc. N_2 at 19°.5 C. and 743.6 mm.

	Calculated for $C_{17}H_{12}N_2O$.	Found.
N	10.77	10.99

Thus prepared, benzoylbenzylmalonic nitrile is a perfectly white, crystalline solid, melting at 100°, sparingly soluble in hot ligroin (70°–80°), and readily soluble in warm ether. It is unaffected by water and by sodium carbonate, but is decomposed by hot alcohol and by aqueous caustic soda, as is established by the following experiments:

a. The substance was heated for half an hour with absolute alcohol in a flask provided with a reversed condenser. Distillation of the alcohol left an oil from which a white, crystalline solid was deposited. The crystal-form and the melting-point (91°) of the solid proved it to be benzylmalonic nitrile. The oil was readily identified as benzoic ether.

b. An ethereal solution of benzoylbenzylmalonic nitrile was treated with caustic soda and the alkaline solution poured at once into dilute sulphuric acid. The product was a mixture of benzoic acid and benzylmalonic nitrile, these were separated by treatment with sodium carbonate, and thoroughly identified.

Brombenzylmalonic Nitrile, $C_6H_5.CH_2\diagdown\atop\qquad\qquad\diagup Br\!\!>C=(CN)_2$. — This substance was prepared by adding 2 grams of sodium benzylmalonic nitrile to an absolute ethereal solution of 1.8 grams (2 atoms) of bromine. After twenty-four hours water was added to dissolve the sodium bromide formed, and the ethereal solution was treated with caustic soda, to insure removal of benzylmalonic nitrile. Distillation of the ether left a slightly colored solid, which was boiled, in ligroin solution, with bone-black, and thus obtained perfectly white. A portion, recrystallized from a mixture of absolute ether and ligroin (40°–60°), gave the following results on analysis:

I. 0.1713 gram gave 18.3 cc. N_2 at 20°.5 and 748.2 mm.

II. 0.0760 gram contained 0.02582 gram Br.

	Calculated for $C_{10}H_7N_2Br$.	Found. I.	II.
N	11.91	12.05	....
Br	34.04	....	33.97

The substance dissolves readily in ether, but is difficultly soluble in water. It crystallizes from alcohol in thin plates with serrated edges, and from ligroin in fine needles, melting

in each case at 119°–120°. Unlike the benzoyl compound brombenzylmalonic nitrile is not affected by aqueous sodium hydroxide. Heated, it distils with decomposition, giving off hydrobromic acid. The distillate is a solid which melts at 70° when recrystallized from alcohol; this is probably a mixture of unchanged substance and benzalmalonic nitrile, whose melting-point is given by Heuck[1] as 87°. Treatment with alcoholic potash converted brombenzylmalonic nitrile, into a dark, thick oil, which refused to solidify, and was not further examined.

Carbethoxybenzylmalonic Nitrile (*Benzyldicyanacetic Ether*), $C_6H_5CH_2\rangle C=(CN)_2$.—Four grams of sodium benzylmalonic nitrile were added to an absolute ethereal solution of 2.48 grams (1 molecule) of chlorcarbonic ether. Reaction set in at once, and was controlled by cooling the mixture with water. After twenty-four hours the sodium chloride produced was filtered off, the ether evaporated *in vacuo*, and the solid residue recrystallized from a mixture of absolute ether and ligroin (40°–60°). The yield was 3 grams, or 60 per cent of the theory. A nitrogen determination of the product gave the following result:

0.1655 gram substance gave 18.6 cc. N_2 at 20° and 740.8 mm.

	Calculated for $C_{13}H_{12}N_2O_2$.	Found.
N	12.28	12.58

Carbethoxybenzylmalonic nitrile is soluble to a slight extent in water and in ligroin (70°–80°), more soluble in ether, and very soluble in alcohol. It crystallizes in large, colorless prisms melting at 44°–45°. Caustic soda acts upon it slowly in the cold, but more readily when hot, evolving ammonia.

Methylbenzylmalonic Nitrile, $C_6H_5CH_2\rangle C=(CN)_2$. — This substance was prepared from both the silver and the sodium salt of benzylmalonic nitrile.

a. 3.7 grams of silver benzylmalonic nitrile were added, in

[1] Heuck: Ber. d. chem. Ges., **28**, 2253.

several portions, to 6 grams (3 molecules) of methyl iodide. The salt hissed like hot iron on coming in contact with the methyl iodide, and the latter was, therefore, diluted with 10 volumes of absolute ether. After the addition of all the silver salt the mixture was warmed to the boiling-point of the ether. The silver iodide formed was then filtered off and the ethereal solution was treated with caustic soda, dried with calcium chloride, and distilled. The ethereal distillate had a faint odor of isonitrile. The residual oil solidified, on cooling, to a colored, crystalline mass, which was obtained perfectly white by treatment, in ligroin solution, with animal charcoal. The yield of crude product was 2.2 grams, or 92 per cent of the theory. The substance was dried *in vacuo* and analyzed with the following results:

I. 0.0984 gram substance gave 0.2804 gram CO_2, and 0.0507 gram H_2O.

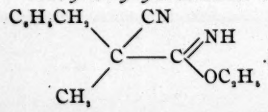
II. 0.0774 gram substance gave 11.5 cc. N, at 21°.5 C. and 747.7 mm.

	Calculated for $C_{11}H_{12}N_2$.	Found. I.	II.
C	77.65	77.70	....
H	5.88	5.73	....
N	16.47	....	16.68

Methylbenzylmalonic nitrile is readily soluble in ether and in alcohol, and slightly soluble in water and in ligroin. It crystallizes from water in needles and from ligroin (70°–80°) in large prisms, melting at 94°–95°.

b. Sodium benzylmalonic nitrile reacts only very slowly with methyl iodide. After several days' standing large, colorless, hexagonal plates separated from the mixture. These melted at 94°–95°, and had all the other properties of the substance made from the silver salt.

Action of Benzylmalonic Nitrile with Methyl Iodide and Alcoholic Sodium Ethylate.

Methylbenzylcyanacetimido Ethyl Ester,  .—3 grams of benzylmalonic ni-

trile, dissolved in absolute alcohol, were treated with an alcoholic solution of 0.45 gram (1 atom) of sodium and with 2.7 grams (1 molecule) of methyl iodide. There was an evolution of heat, and the mixture became neutral in twenty minutes. The alcohol was then distilled and the residue treated with water and extracted with ether. After treatment with caustic soda the ethereal solution was dried with chloride of calcium, and the ether evaporated. An almost colorless oil remained, which distilled at reduced pressure (170° at 22 mm.) without decomposition. The yield was 3.5 grams, or 85 per cent of the theory.

An analysis gave the following results:

I. 0.1750 gram substance gave 0.4624 gram CO_2, and 0.1198 gram H_2O.

II. 0.1555 gram substance gave 18.2 cc. N_2 at 21° and 742.6 mm.

	Calculated for $C_{13}H_{16}N_2O$.	Found. I.	Found. II.
C	72.22	72.06	....
H	7.41	7.61	....
N	12.96	....	13.08

The product obtained in the case of the Conrad-Limpach reaction is, therefore, not the nitrile, but the imido ether.[1] This is a faintly aromatic, colorless oil, insoluble in water and in caustic soda. When its alcoholic solution is treated with concentrated hydrochloric acid a white precipitate of ammonium chloride is instantly formed. After standing six months the oil became so viscous that it could hardly be poured, yet all attempts to make it solidify were unsuccessful. The properties of the substance had also changed; ether dissolved it only partially, leaving a white, amorphous solid. That the imido ether obtained in the reaction described above is formed from the nitrile by the addition of alcohol is proved by the behavior of methylbenzylmalonic nitrile with sodium ethylate. Methylbenzylmalonic nitrile (1.2 grams) dissolved in absolute alcohol was treated with an alcoholic solution of 0.16 gram (1 atom) of sodium. No change was noticed, except that the solution became slightly colored. After standing at

[1] Cf. Nef: Ann. Chem (Liebig), **287**, 273, 315–8, 343. Also Hesse: This JOURNAL, **18**, 744.

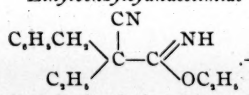
the ordinary temperature over night the mixture was poured into water and the separated oil extracted with ether. A substance was obtained which boiled at 156° at 9 mm.; weight, 1.15 grams, or 75 per cent of the theory.

A nitrogen determination resulted as follows:

0.2066 gram substance gave 24.3 cc. N_2 at 21° and 746.8 mm.

	Calculated for $C_{13}H_{14}N_2O$.	Found.
N	12.96	13.22

This substance is identical in every respect with the imido ether described above.

Ethylbenzylcyanacetimido Ethyl Ester,  .—This compound was prepared from both ethyl and benzylmalonic nitrile.

a. 2 grams ethylmalonic nitrile, dissolved in absolute alcohol, were treated with an alcoholic solution of 0.5 gram (1 atom) of sodium and with 2.7 grams (1 molecule) of benzyl chloride. The temperature of the mixture rose to 50°. After the distillation of the alcohol, water was added to the residue and the separated oil extracted with ether, washed with sodium hydroxide, and dried with calcium chloride. Distillation of the ether left a product boiling at 170° at 22 mm.; weight, 3.5 grams, or 71 per cent of the theory.

A nitrogen determination gave the following result:

0.2339 gram substance gave 25.4 cc. N_2 at 19° and 744.5 mm.

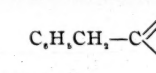
	Calculated for $C_{14}H_{18}N_2O$.	Found.
N	12.18	12.28

This substance is decomposed by concentrated hydrochloric acid, like all imido ethers, with separation of ammonium chloride. It is colorless when freshly prepared, but becomes brown on standing.

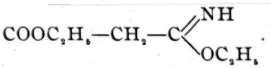
b. 1 gram benzylmalonic nitrile, dissolved in absolute alcohol, was treated with an alcoholic solution of 0.13 gram (1 atom) of sodium and with 2 grams (2 molecules) of ethyl

iodide. A product (0.9 gram, *i. e.*, 75 per cent of the theory) boiling at 171° at 23 mm., and identical in its properties with the imido ether described under *a* was obtained.

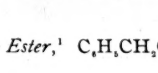
Finally, there is appended here a description of a convenient method of preparing *phenylacetimido ether*,



and *monimidomalonic ether*,



These substances are of interest especially because analogous compounds have been assumed as intermediate products in the conversion of malonic nitrile and its monalkylated derivatives into salts. A study of them will, therefore, be continued in this laboratory. Their behavior toward metals, amines, sodium ethylate, and alkyl iodides deserves special investigation.

Phenylacetimido Ethyl Ester,[1]  . — The hydrochloride of this substance was made from benzyl cyanide by the method of Pinner, and was obtained at first as a colorless oil, which solidified with much difficulty. The salt is perfectly white and odorless and very soluble in water, which decomposes it into phenylacetic ether and ammonium chloride.

The free imido ether was prepared from the hydrochloride by the method of Bushong :[2] 10 grams of the salt were added to an excess of 10 per cent sodium hydroxide cooled to 7° C., and the separated oil was taken up at once with ether and dried with calcium chloride. Distillation of the ether left a colorless substance, boiling at 105°–106° at 10 mm. pressure. The yield was 6.9 grams, or 84 per cent of the theory.

A nitrogen determination gave the following result :

0.1538 gram substance gave 12 cc. N_2 at 23° C. and 752.6 mm.

[1] Cf. Lückenbach : Ber. d. chem. Ges., **17**, 1421.

[2] This JOURNAL, **18**, 490.

	Calculated for $C_{10}H_{13}NO$.	Found.
N	8.59	8.75

The imido ether is insoluble in water and in aqueous alkalies. It distils at ordinary pressure with slight decomposition into alcohol and benzyl cyanide. Treated, in absolute ethereal solution, with metallic sodium, the imido ether gave a white, amorphous precipitate, which was not further examined.

Monimidomalonic Ether,[1] $CH_2\begin{matrix}C(NH)OC_2H_5\\COOC_2H_5\end{matrix}$.--The hydrochloride of this substance was made from cyanacetic ether by the method of Pinner. The salt was obtained as a colorless oil, which solidified, when shaken with cold ether, to a white, crystalline mass. It is soluble in cold water without decomposition, but on heating malonic ether is set free.

The free imido ether (made by adding the hydrochloride to cold 10 per cent sodium hydroxide) is a colorless oil, distilling at reduced pressure without decomposition. Heated at ordinary pressure, however, to 165°, it is decomposed into alcohol (75 per cent of the theoretical amount was obtained), and a thick, pasty mass, India-red in color, and insoluble in ether and in alcohol.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE PHENYLHYDRAZONES OF BENZOIN.

BY ALEXANDER SMITH.

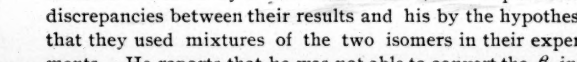
Some years ago,[2] in association with Mr. J. H. Ransom, I described the preparation and properties of a substance formed by the interaction of phenylhydrazine and benzoin which differed in physical properties, although not in chemical properties or composition, from the phenylhydrazone of Pickel.[3] The new compound, being more soluble, somewhat less stable, and of lower melting-point than the old one, was characterized as the β-form. In accordance with the view

[1] Cf. Oppenheimer: Ber. d. chem. Ges., **28**, 478.
[2] This JOURNAL, **16**, 108.
[3] Ann. Chem. (Liebig), **232**, 229.

then (and now) prevailing in regard to such cases, the forms were held to be stereoisomers :

α-Phenylhydrazone, m. p. 158°–159°. *β*-Phenylhydrazone, m. p. 106°.

The relation between these bodies has recently[1] been investigated by Freer. His results are, in several important particulars, in conflict with those of Smith and Ransom. He did not succeed in obtaining the substances in pure form by the methods indicated by Smith and Ransom, and explains the discrepancies between their results and his by the hypothesis that they used mixtures of the two isomers in their experiments. He reports that he was not able to convert the *β*- into the *α*-form by boiling with excess of phenylhydrazine in alcoholic solution. He also finds that the bodies behave differently towards benzoyl chloride and nitrous anhydride, founding on this the conclusion that they are not stereoisomers, but structurally different. The *β*-form he classes with the hydrazo-derivatives, the *α*-form with the hydrazones :



From the action of benzoyl chloride on the *β*-form he obtains a *γ*-phenylhydrazone (m. p. 162°) which he hesitates to class definitely as a stereoisomer of the *α*-body.

Being unable to account for these observations, I have re-examined the properties of the substances. I find that there is nothing to modify in the statements of Smith and Ransom called in question by Freer, that the supposed differences in the chemical behavior of the *α*- and *β*-forms are non-existent, and that the new *γ*-phenylhydrazone is not a phenylhydrazone at all.

Transformation of the β- into the α-Form.

This was accomplished by Smith and Ransom[2] by boiling

[1] This JOURNAL, **21**, 22 and 45. [2] *Ibid.*, 115.

the pure β-phenylhydrazone in alcoholic solution with two molecular proportions of phenylhydrazine for eighteen hours. A 50 per cent yield of the α-form was easily obtained. Freer states[1] that when he repeated this experiment with 2 grams of the "pure" β-phenylhydrazone, only 0.05 gram of the α-body was produced. Our result is explained by the naive assumption that we used a mixture of the β- and α-forms in all our work, and has simply recovered the latter. This hypothesis is inconsistent with Freer's own statement[2] that the product of the interaction of phenylhydrazine and benzoin, by the method used by us in preparing the β-body, contains 1 part of the α-body to 6 parts of the β-body. This would indicate that, even without purification, our β-substance could not have contained more than 15 per cent of the α-form. It is needless to say that the β-substance we used was always tested most rigidly as regards freedom from the α-form before use.

Fortunately, there was still in my possession a portion of the β-phenylhydrazone originally used in this work, as well as a sample of the α-form made from it by transformation. Beyond a slight coloration, they had remained unaltered by keeping for five years. The β-body was found still to be perfectly pure. It dissolved instantly and completely in cold glacial acetic acid (the test for the absence of the α-modification given by Freer himself), and fulfilled also the more rigid tests of purity we had habitually applied. The α-body still melted at 158°–159°.

The transformation has now been repeated several times successfully by following the directions originally given by Smith and Ransom. The β-body used was perfectly homogeneous under the microscope, dissolved instantly in cold glacial acetic acid, and melted sharply at 106°. The phenylhydrazine (Kahlbaum's) was purified for use by freezing one-third of a large quantity, rejecting the unfrozen part, melting the crystals, and freezing one-third of the resulting liquid. The only difficulty encountered was that, in one case when a large flask connected with an upright condenser was used, a portion of the material was oxidized to the osazone of benzil,

[1] This JOURNAL, 21, 49. [2] *Ibid.*, 48, foot-note.

through the exposure of a larger surface than usual to the air. All danger from this source may be avoided by using a sealed tube. One experiment made in this way, with a shorter allowance of time than that formerly given, may be quoted.

The β-phenylhydrazone (2 gr. = 1 mol.) and phenylhydrazine (1.4 gr. = 2 mol.) were dissolved in absolute alcohol (30 cc.) and heated at 100° for eight hours. The resulting pale-yellow liquid was concentrated on the water-bath and then left to evaporate spontaneously. The residue solidified almost completely to a mass of crystals which were freed from most of the adhering oil by pressing on a filter and spreading on a porous tile. This impure product weighed 1.5 grams. Even in this crude condition it softened at about 106°, but did not melt completely till a much higher temperature was reached. By agitation with cold glacial acetic acid for a few minutes the unchanged β-form, along with a small portion of the α-body, was removed. The undissolved material, when dry, weighed 0.65 gram and melted at 157°–158°. As an additional safeguard, 1 gram of the β-phenylhydrazone used in this experiment was agitated with the same proportion of cold glacial acetic acid for about the same time. It dissolved completely.

The γ-Phenylhydrazone of Freer.

By the action of benzoyl chloride on an ethereal solution of the β-phenylhydrazone, in the cold, Freer obtained a substance forming plates, with mother-of-pearl luster, melting at 162°. This, along with the hydrochloride of a base, whose nature was not determined, was deposited during the course of two days. The mother-liquor, on evaporation, was found to contain benzil and unchanged benzoyl chloride and tar.

This experiment was repeated and the substances described by Freer were obtained with ease. The hydrochloride of a base turned out to be largely ammonium chloride mixed with a little of the hydrochloride of a solid base which was not further examined. Freer's analysis and molecular weight determinations assign the formua $C_{20}H_{18}N_2O$ to the body melting at 162°. He regards it therefore as a new isomer and

names it the γ-phenylhydrazone of benzoin. The α- and γ-forms he considers true phenylhydrazones and the β-body a hydrazo-derivative.

A brief examination of the substance sufficed to raise suspicion that it was not a phenylhydrazone at all. It distilled without decomposition. It could be boiled with benzaldehyde over the naked flame without interaction. It was heated in a sealed tube with concentrated hydrochloric acid for two hours at 100°, and a large part found to crystallize out of the hot acid in radiating needles, very unlike the ordinary plate form, having suffered, however, no chemical change. Now the α- and β-phenylhydrazones are decomposed by heat, react with benzaldehyde forming a substance[1] melting at 215°–216°, and turn to tar when left in contact with concentrated hydrochloric acid even in the cold.

At this point it was observed that the percentage of nitrogen given by Freer (9.42) was not in agreement with the data accompanying it (which gave 8.93, over 30 per cent caustic potash, 9.2 dry), and another estimation of the nitrogen was made. The percentage found was 7.2. This, with the combustion figures given by Freer, suggested $C_{13}H_{11}NO$ as a probable formula. The molecular weight of this body being much smaller than the values observed by Freer, two determinations of this constant were made in boiling alcohol by a modification of Walker and Lumsden's method[2] devised by Dr. McCoy. The following table shows the results of Freer's and my own measurements:

0.1667 gram substance gave 14 cc. nitrogen at 31° and 743 mm. (Freer).

0.2419 gram substance gave 15.8 cc. nitrogen (over 30 per cent KOH) at 24° and 743 mm. (Smith).

Molecular weight in solution in absolute alcohol (Smith).

	Substance. Gram.	Volume of solution. cc.	Rise.
I.	0.432	20.4	0.148°
II.	0.432	22.0	0.144°

[1] This JOURNAL, 16, 114.

[2] J. Chem. Soc., 73, 502. The description of Dr. McCoy's modified apparatus will be published shortly.

	Calculated for $C_{20}H_{18}N_2O$. γ-Phenylhydrazone.	Found. (Freer.)	Recalc. from Freer's data.	Calc. for $C_{13}H_{11}NO$.	Found. (Smith.)
C	79.43	79.13	....	79.19	....
H	5.96	6.09	....	5.58	....
N	9.27	9.42	8.93	7.11	7.20
Mol. wt. I.	302.0	298.0		197.0	223.0
Mol. wt. II.		339.0			213.0

The composition, molecular weight, and melting-point being found to agree with those of benzanilide (m. p. 161°–162°), a little of the substance was mixed with a specimen of benzanilide, obtained from Kahlbaum, and the melting-point of the mixture was determined. No lowering in the melting-point, such as the introduction of a foreign substance would have caused, was observed, and the resolidified mixture, on being warmed once more, still melted sharply at 162°. To increase the certainty of this conclusion, a molecular-weight determination was made, with Kahlbaum's benzanilide, by McCoy's method:

	Substance. Gram.	Volume of solution. cc.	Rise.	Molecular weight found.
I.	0.626	15.2	0.299°	215
II	0.626	17.9	0.262°	208

A slight degree of association was to be anticipated in the case of benzanilide (mol. wt. 197) and was observed with both specimens to an equal extent, as the above results show.

This simple solution of the difficulty relieves us at once of the γ-form, and at the same time throws light on the formation of benzil and of the ammonia referred to above. The elements of water required for the change were not obtainable directly, since absolute ether was used as a solvent, and were probably taken from part of the benzoin. This would explain the formation of the considerable amount of tar mentioned by Freer and observed by me. The following equation represents the action in outline:

$$C_6H_5.CH(OH).\underset{\|}{\overset{N.NHC_6H_5}{C}}.C_6H_5 + C_6H_5.CO.Cl\ (+H_2O) \rightarrow C_6H_5.CO.CO.C_6H_5 + NH_4Cl + C_6H_5.CO.NHC_6H_5.$$

β-Phenylhydrazone or Hydrazo Derivative?

According to Freer,[1] phenylhydrazine derivatives which can be oxidized to azo-bodies and react with benzoyl chloride forming either diacyl substitution-products, or "bodies from which dibenzoylphenylhydrazine can be obtained," are hydrazo compounds. On the other hand, "true hydrazones, which, of course, cannot be oxidized to bodies with the azo-structure, are either not acted on at all by acyl chlorides or they are converted into monoacylated derivatives or into monosubstituted phenylhydrazines." Freer's experimental results along these lines led him to classify the phenylhydrazones of acetone and acetophenone under the former head, and those of pyruvic ether and benzophenone under the latter.

Freer did not obtain any simple azo-compound, however, or, in the benzoyl chloride reaction, any other evidence that the β-phenylhydrazone of benzoin was similar to the hydrazides of acetone or acetophenone. Yet, in spite of this, he considers that "it is probably the hydrazo compound" (p. 53). The sole ground for this reasoning *per saltum* appears to be the bare fact that the α- and β-bodies behave differently in presence of benzoyl chloride and when treated with nitrous anhydride. With benzoyl chloride and the α-form no action at all was observed by Freer in the cold; the different behavior of the β-form is discussed above. With nitrous anhydride in dry ether, the β-form gave a red body of the nature of an addition-product with elimination of some water, while the α-form gave only a white substance bearing not even the remotest physical resemblance to the azo-compounds. These results, if confirmed by further work, might form a ground for believing that the substances are "structurally different," but surely not for deciding that the β-form is a hydrazo-compound.

I had no desire to take part in the task of determining the structures of hydrazones, and, in any case, should naturally avoid interfering with Freer's field of work. But my acquaintance with the properties of the two bodies in question made it difficult for me to believe that they would behave differently towards reagents like benzoyl chloride and nitrous

[1] *Ibid.*, 19.

anhydride. At the time of the discovery of the β-form, the hydrazo-structure seemed scarcely probable in view of its stability in air. The hydrazo-compounds, from acetone and acetophenone, both become red and finally tarry in a very short time. The β-body showed no such tendency. This conclusion is only strengthened by the fact, mentioned above, that a period of five years, even, has not affected its purity. The actions of benzoyl chloride and nitrous anhydride were therefore tried with the α-body. The details are given below. From the α-body exactly the same substances were obtained, in about the same quantity and proportions, as from the β-body. This can hardly be explained on the assumption that the products arose from admixture of some of the β-derivative. A specimen of the α-phenylhydrazone, melting sharply at 158°–159° (the m. p. of the pure body originally published by me and accepted by Freer) could not have contained such a proportion of the β-body (m. p. 106) as to give as good yields as the β-body itself. I can draw no other conclusions than that the products, formed from the β-body in the one case, came from the α-body in the other.

Action of Benzoyl Chloride on the α-Phenylhydrazone of Benzoin.

The exact proportions and conditions used by Freer (p. 45) for the β-body were observed. The α-body (3.5 grams) was dissolved in absolute ether and an equal amount of benzoyl chloride was added to the cold solution. The turbidity was somewhat longer in making its appearance than in the case of the β-body. But after 2–3 days the yellowish, crystalline substance deposited ceased to increase in quantity. The ethereal liquid was poured off, and the solid washed with a little pure ether, and then, to dissolve the hydrochloride, with water. The addition of sodium hydroxide to the aqueous extract liberated ammonia, which was distilled off and found, by titration, to be equivalent to 0.11 gram of ammonia. A small amount of a solid base also separated. The remainder of the solid body was recrystallized from alcohol and found to melt at 162° and be identical in physical properties with the benzanilide formed from the β-phenylhydrazone. A further quantity of the same substance was isolated from the mother-

liquor after evaporation. The total amount obtained from 3.5 grams of the hydrazone was 1.3 grams. The mother-liquor gave also unchanged benzoyl chloride, benzil (1 gram) and uncrystallized tar. From 5 grams of the β-body Freer obtained 2.7 grams of the "γ-phenylhydrazone" (benzanilide) and 1.7 gram of benzil, so that the proportions for the α-body are approximately the same. This reaction gives, therefore, no ground for inferring any difference in structure in the two forms of the phenylhydrazone.

Action of Nitrous Anhydride on the Phenylhydrazones.

In Freer's experiment the β-phenylhydrazone was dissolved in absolute ether and cooled by a freezing-mixture. He allowed nitrous anhydride to pass in slowly until a transitory red tint gave place to a green color. The solution was then agitated with potassium carbonate solution. A red crystalline substance soon appeared in the ether which, when purified, melted at 137° with decomposition. Freer assigns to this substance the formula $C_{26}H_{14}N_4O_6$.

On treating the α-body in the same way, Freer obtained a dense, white crystalline precipitate, which converted the ethereal solution into a thick paste. The nature of this substance was not determined. He adds, "I was unable to obtain any of the red body derived from the β-hydrazone, on using the *pure* α-body, but I did observe its formation when using a sample prepared according to Smith and Ransom's directions. This result was probably due to the fact that some of the β-variety was present in the latter instance." The italics are Freer's.

The writer has been more fortunate, as from 5 grams of the *pure* α-body, purified according to Freer's directions, he had no difficulty in obtaining 1.8 grams of the same red substance in the first crop of crystals. The mother-liquor was not examined. Freer got 3.3 grams in all. After recrystallization from boiling benzene (solubility 1 in 20), the substance melted at 138° with decomposition. It was identical with the product from the β-body (first crop of crystals equals 1.2 gram), made for the purpose of comparison. In both cases a slight white precipitate made its appearance during the passage of the nitrous anhydride, but in neither case did the amount exceed a few milligrams.

These results show that either both phenylhydrazones of benzoin have the hydrazo-structure, or that, contrary to Freer's assumption, the formation of red bodies of this nature with nitrous anhydride may take place with true hydrazones. In the latter case, no ground for assigning a hydrazo-structure to either of the phenylhydrazones of benzoin would have survived closer examination.

To settle this point, the phenylhydrazone of benzophenone, a substance which Freer regards as undoubtedly a true phenylhydrazone, was subjected to the action of nitrous anhydride under conditions exactly the same as those described above. No white precipitate was observed. The ethereal solution deposited the expected red body (0.8 gram from 1 gram of the substance). It was very difficultly soluble and, when recrystallized from xylene, melted at 231°.

To avoid trespassing on Freer's territory the work was broken off at this point. For my purpose, it was sufficient to have shown that my former observations were correct, and that a consideration of all the facts leaves nothing which is inconsistent with the conclusion that the two phenylhydrazones of benzoin are stereoisomers.

In conclusion, I wish to express my thanks to Dr. H. N. McCoy for making the analysis and molecular weight determinations, as well as for assisting in the work described in the last section.

CHICAGO, June 7, 1899.

NOTES OF STUDENT WORK FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF VIRGINIA.

COMMUNICATED BY F. P. DUNNINGTON.

XXI.

168.—THERMAL EFFECTS OF THE DILUTION OF SOME SALTS.

BY F. P. DUNNINGTON AND T. HOGGARD.

It is well known that solutions of certain acids and salts when diluted with water occasion rise or fall of temperature. Much work upon this subject has been conducted by Regnault,

Favre, Thomsen[1] and others and more recently by Prof. S. U. Pickering in his elaborate study on the nature of solutions. G. Lemoine has studied solutions of lithium chloride.[2] This work upon solutions of salts appears to have been confined chiefly to the determination of the thermal changes upon promptly dissolving salts in a large amount (100—1000 molecules) of water, which of course gives only the algebraic sum of all the changes of liquefaction, solution, and dilution. It therefore appeared desirable to examine a number of dissolved salts after the same manner as has been employed with the acids[3] to ascertain what classification, if any, they may show in this respect. Each salt was dissolved in the least integral number of molecules of water in which it could be readily dissolved at ordinary temperatures, 20°–25° C., and then, as each successive molecule of water was added to the strong solution, the calories evolved or taken up (+ or —) were estimated; a calorie being taken as the heat required to change one gram of water one degree centigrade in temperature. It is to be noted that the solutions used were not actually saturated, but had enough additional water to amount to a whole number of molecules before the measurements were begun, so that the change was not measured up to the point at which it is at a maximum.

The observations were made in thin beakers (in most cases) protected by cotton wool, using a mercury thermometer which could be read to $\frac{1}{20}$ degree centigrade, and all temperatures kept within two or three degrees of that of the atmosphere. The water to be added was brought each time to the temperature of the solution, or estimation made for the temperature of each liquid. The thermal effect of the beaker and thermometer was ascertained by experiments with water, and allowance also made for the specific heat of the dissolved salts.[4] In most cases the amount of the salt taken was its molecular weight in grams as given in the table, and where otherwise, the results are calculated to this amount. The heat developed is expressed in calories obtained from the

[1] Handbuch. d. Physik., Dr. A. Winkelmann (1896), Vol. II. p. 636.
[2] Compt. rend., 1897, 125, 603.
[3] Watts' Dictionary (1875), Vol. III, p. 109.
[4] Phys. Chem. Tabellen, pp. 333; Landolt and Börnstein.

gram-molecule of each salt. For example: lithium chloride, 42.5 grams is dissolved in four molecules (*i. e.* 72 cc.) of water, and the addition of the fifth molecule (18 cc.) of water develops a gain of 678 calories, the sixth gives 422 calories, the ninth, 141; the tenth and eleventh, 172 ($\frac{172}{2}=86$) and the twelfth, thirteenth, and fourteenth, 159 ($\frac{159}{3}=53$). Thus it will be seen that the blanks at the top of the table indicate the water required to effect solution, and the blank spaces below are followed by a figure which gives the average for that molecule and the blanks preceding it.

The first half of the table gives the results for salts which give only a rise in temperature; the second half gives results showing a fall in temperature. Because no refined method of obtaining these figures was available, they can only be considered as approximate, yet they show very clearly that most of the thermal change developed upon dilution of strong solutions takes place upon the addition of the first few molecules of water. Notably is this the case with sodium bromide, calcium chloride, magnesium nitrate, and potassium chloride.

On the other hand calcium nitrate presents a prominent exception to the other salts examined, in that it first evolves heat and subsequently absorbs it. In this one instance the observations were continued down to the 55th molecule of water and it seems probable that the slight irregularities shown are due to errors in observations, such as may be present in the other determinations also.

The special salts selected were taken because, of those which dissolve in a comparatively small amount of water, they only were available. It is to be noted that the highly deliquescent salts are those which afford most heat at the early stage of diluting; beyond this, there does not appear any generalization of the salts which act similarly.

CALORIES OBTAINED UPON THE ADDITION OF EACH MOLECULE OF WATER TO THE DISSOLVED SALTS.

Molecules of water.	Ammonium acetate.	Lithium chloride.	Sodium bromide.	Magnesium nitrate.	Calcium chloride.	Magnesium chloride.	Strontium chloride.
	77	42.5	103	148	111	95	158
1							
2							
3							
4	119						
5	103	678					
6	95	422		76			
7		230		37			
8	60	183		33			
9		141					
10	52						
11		86					
12	44			7	508		
13			223		123	370	
14		53	79			268	
15					66		64
16	30			1		109	23
17							
18		29	6			81	43
19					21		
20	27						25
21							
22		1	3			24	
23							
24							23
25					1		
26						14	
27							
28							
29							
30			2			2	14

CALORIES (—) OBTAINED UPON THE ADDITION OF EACH MOLECULE OF WATER TO THE DISSOLVED SALTS.

Calcium nitrate.	Ditto + $30H_2O$.	Ammonium nitrate.	Sodium nitrate.	Ammoniumchloride.	Sodium chloride.	Potassium chloride.	Potassium bromide.	Potassium iodide.
164	—	80	85	53.5	58.5	74.6	119	166
		—290						
	—36	—205						
		—172						
								—160
		—122	—87					
+131								
+ 41	—30	— 97	—50		—11		—139	— 48
+ 21					—11		— 73	
+ 8		— 68		—75	—12		— 77	
— 5				—54	—10	—221		
— 22			—16	—51		— 33	— 21	
— 29	—20			—31	—14			
— 53		— 46				— 0	— 23	— 11
— 34				—20	— 8			
			— 9	—18				
— 39							— 13	
	— 15	— 28		—23		— 0		
— 47								
				—15	— 1		— 8	— 6
— 36		— 19	— 6	—11				
	— 6				— 2			
							— 0	
	— 21					— 0		
— 45			— 1					— 1

UNIVERSITY OF VIRGINIA,
May, 1899.

169. ANALYSIS OF EMERY FROM VIRGINIA.

By W. W. Miller, Jr.

This mineral was received from the late James F. Slaughter, Esq., of Lynchburg. It occurs in a heavy ledge near Whittle's, on the line of the Southern Railroad, in Pittsylvania Co. It is a black crystalline mass; magnetic; polar; sp. gr. = 4.205; emits the characteristic odor of emery; hardness, on edges = 8; infusible; and affords no loss upon intense ignition.

It may be dissolved by fusion with sodium acid sulphate. A portion heated to 450° C. with sulphuric acid in a sealed tube afforded estimations of silica and ferrous oxide. The rest of the analysis was made with a solution obtained by the successive action of hydrofluoric acid and sulphuric acid, showing the following composition:

		Molec. ratio.
Alumina	56.74	55.63
Ferric oxide	15.50	9.69
Ferrous oxide	20.77	28.85
Silica	0.68	
Titanic oxide	1.86	
Soda	3.95	
	99.50	

Soda is found in many of the silicates associated with emery, but in smaller amount than will account for its occurrence here. The amount of ferrous oxide in excess of that required to form magnetite is apparently present as hercynite, $FeAl_2O_4$. Omitting the silica, titanic oxide, and soda, the remaining constituents correspond to a mixture of magnetite 22.48 per cent, hercynite 33.34 per cent, and corundum 37.16 per cent. A thin section reveals the presence of two minerals other than the magnetite.

It seems most probable that the soda replaces some ferrous oxide in forming hercynite so that the amount of alumina existing as corundum is even less than that stated above.

While the substance is very tough and hard, it has not sufficient erosive power to give it value as emery. The

emery of Chester, Mass., is similar to this in appearance, but Dr. J. Lawrence Smith considered that in it the whole of the alumina occurs as corundum and the iron as magnetite and that no hercynite is present. Probably the latter difference between these specimens accounts for the difference in erosive power.

UNIV. OF VA., June, 1898.

170. PRESERVATION OF HÜBL'S REAGENT.

BY RANDOLPH BOLLING.

One of the most satisfactory tests for the identification of certain fatty oils is that of Baron Hübl, consisting of a determination of the amount of iodine absorbed by the oil.[1]

The solution of iodine employed is known to lose strength rapidly; it was therefore proposed to determine the amount of this change under varying conditions, hoping thereby to obtain some improvement upon this feature of the test.

A solution was made up according to the formula given, with iodine 25 grams, mercuric chloride 30 grams, and strong alcohol (91 per cent) 1 liter. Portions of this were kept under different conditions:

Portion A—1. In clear glass, $\frac{1}{8}$ to $\frac{1}{4}$ filled, loosely stoppered, repeatedly opened and exposed to daylight.

" " 2. In clear glass, filled, closely stoppered, exposed to daylight.

" " 3. In amber glass, filled, closely stoppered, kept in darkness.

Another solution, B, was similarly made, but using absolute alcohol, and divided thus:

Portion B—2. Filled, closely stoppered, exposed to daylight.

" " 3. Filled, closely stoppered, kept in darkness.

In making the tests, 5 cc. of the solution were properly diluted and titrated with a standard solution of sodium thiosulphate. These solutions were thus tested as indicated during the first week, and then weekly. The following table gives the amount of free iodine found in 5 cc. at each test.

[1] J. Soc. Chem. Ind., 3, 641.

Free Iodine Present in 5 cc.

Iodine dissolved.	A1. 0.1250	A2. 0.1250	A3. 0.1250	B2. 0.1250	B3. 0.1250
After 3 hours	0.1137	....	....	0.1149	....
" 2 days	0.1106	....	....	0.1125	....
" 4 "	0.1006	....	....	0.1106	....
" 7 "	0.0992	0.0980	0.0980	0.1095[1]	0.1052
" 2 weeks	0.0835	0.0883	0.0956	0.1016	0.1041
" 3 "	0.0844	0.0835	0.0876	0 0978	0.0992
" 4 "	0.0823	0.0799	....	0.0932	0.0847
" 5 "	0.0774	0.0774	0.0811	0.0932[1]	0.0883
" 6 "	0.0750	0.0738	0.0786	0.0895	0.0932
" 7 "	0.0702	0.0690	0.0738	0.0859[1]	0.0907[1]
" 8 "	0.0641	0.0629[1]	0.0702	0.0811[1]	0.0835[1]

It appears, therefore, that the alteration of this solution is very rapid and is delayed to but a small extent by employing absolute alcohol or by excluding air and light. There is full reason for the precaution of redetermining the strength of the solution whenever it is employed.

UNIV. OF VA., June, 1898.

171. DEHYDRATION OF CRYSTALS OF SODIUM PHOSPHATE.

BY T. C. WHITLOCK AND C. E. BARFIELD.

There is little definiteness, and some discrepancy, in the statements made as to the expulsion of water from crystallized disodic-hydrogen phosphate. We are told[2] "These crystals at 30° to 40° C. gradually give off their water of crystallization, and when heated to redness give off their basic hydrogen." Also by Fresenius:[3] "The water of crystallization is expelled by heating at 100° to a constant weight, and that of constitution by ignition."

It was therefore proposed to ascertain more exactly the conditions under which we may expel the water of crystallization and of constitution. These results are reached from the work of several students in this laboratory, many determinations, showing the gradual loss of water as the temperature was raised, are not given.

The following were obtained by Messrs. Whitlock and Barfield:

[1] Began a new bottle kept under similar conditions, but previously unopened.
[2] Watts' Dictionary (1871), Vol. IV, p. 580.
[3] Quant. Anal., Braunschweig, 1887, S 781.

By reason of the readiness with which these crystals effloresce, the extent of dehydration was checked by a final ignition.

If the salt is put immediately into the steam-bath the crystals will melt and then the dehydration may require twelve hours or more.

The salt was gently heated on top of the steam-bath for from five to ten minutes, then in the bath (96° C.) for fifteen minutes, and then the loss

In	3	hours	at	150°	C.	was	60.25 per cent
"	1	hour	"	170°	"	"	60.22 "
"	1	"	"	180°	"	"	60.30 "
"	1	"	"	190°	"	"	60.33 "
"	1	"	"	200°	"	"	60.26 "
"	1	"	"	200°	"	"	60.35 "

At lower temperatures it required much longer to attain the same loss. The salt contains 60.343 per cent of water of crystallization.

The water of constitution was determined by further heating the above dehydrated residues. Portions were exposed for one hour to gradually increasing temperatures; *viz.*, 180°, 190°, 200°, 210°, 215°, 220°, with no loss. These, when heated severally to 230°, 240°, 250°, gave a little loss. In order promptly to remove this water, "dehydrated residues" were heated and the loss

In	1	hour	at	270°	C.	was	1.80 per cent
"	2	hours	"	270°	"	"	2.47 "
"	1	hour	"	275°	"	"	2.44 "
"	1	"	"	280°	"	"	2.23 "
"	1	"	"	290°	"	"	2.43 "
"	1	"	"	300°	"	"	2.48 "

Hence we see that the water of crystallization may be removed below 220° and (after efflorescence) at 180° in one hour, and that the water of constitution begins to be lost at 230°, and may be removed in one hour at 300°, or more promptly by a low red heat.

UNIV. OF VA., June, 1897.

172. EXAMINATION OF A SANDSTONE FROM AUGUSTA COUNTY, VIRGINIA.

By W. W. Miller, Jr.

About one-half mile east of Basic City there passes a line of hills, which rise at the foot of the western slope of the Blue Ridge and consist of Lower Cambrian Quartzite. The track of the Chesapeake and Ohio Railroad passes by one of these hills, and material from it is largely used by this railroad for ballast. This hill is covered with a coating 40 feet or more in thickness of the same composition as the rest of the hill, but consisting of a mass of angular fragments, mostly 2 or 3 inches in dimensions and graduating to a dust. This shattering seems to be the work of frost. In seams between the fragments there is a small amount of clay mixed with finely divided silica, which also is seen under the microscope to be in angular fragments. The deposit is readily loosened with a pick, and is then loaded upon cars for ballast. When this material is sifted to three or four sizes, laid, and beaten down for a pathway, with the coarser lumps at the bottom and finer on top, it soon becomes firm and compact, and yet allows rain to soak through it promptly. The peculiar property which it possesses of thus becoming compact when dumped and left undisturbed for a short time, led to seeking an explanation of this fact through the following analyses of both the clay and the rock.

The fine powder was brought into solution by repeated fusion with sodium acid sulphate and treatment with hydrofluoric acid. The alkali was determined by Dr. J. Lawrence Smith's method. The following results were obtained :

	Clay.	Rock.
Alumina	24.23	2.37
Titanic oxide	0.94	0.00
Ferric oxide	3.57	0.46
Magnesia	1.25	0.00
Potash	4.04	0.00
Soda	0.77	0.19
Water, lost at 100° C.	0.49	0.00
" " by ignition	4.83	0.26
Silica, amorphous, free	0.53	0.00
" cryst. and combined	63.68	by diff. 96.72
	99.29	100.00

The clay was treated with hydrochloric acid, and the filtrate proved to contain no alkali. Hence it appears that the alkali is contained in form of a silicate. There are, moreover, geological reasons for stating that feldspar is being formed and silica altered to quartzite. As these results present no chemical explanation of the peculiar property, most probably it is due solely to physical causes. Being in sharp, angular pieces with rough fracture, these readily hold in place when once packed, the finer portion filling in the cavities. Moreover, this packing takes place most readily when compacted by use when the pathway is wet.

UNIV. OF VA., May, 1899.

173. SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE.

BY J. C. LONG.

In the estimation of lead as sulphate, occasionally it is desirable to bring it into solution so as to separate and purify it for weighing. Among the solvents to be employed for this purpose, a solution of ammonium acetate is most recommended. The action of this solvent, though often mentioned, is not fully described, and the only figure given in Storer's "Dictionary of Solubilities" is that of Bolley, stating that "at 12.5° C. one part of lead sulphate is soluble in 47 parts of a solution of ammonium acetate having sp. gr. = 1.036" (= 18 per cent). Hence it appeared desirable to define more closely the conditions under which this operation is best conducted.

A preliminary test was made with portions of pure precipitated lead sulphate, which indicated that it required for its solution about 10 parts of a solution containing 56 grams of ammonium acetate in 100 cc. Then taking 0.5 gram of lead sulphate and 5 cc. of the above solution in each of several test-tubes, to these there was added of

Water:	0	1	2	3	4	5	6	7 cc. giving
Approx.:	56	46	40	35	31	28	25	23 grams in 100 cc.

With agitation, these were digested at 100° C., and it appeared that the solution of 35 "volume per cent" was the first to leave no residue.

An excess of lead sulphate was boiled with solutions of ammonium acetate of various strengths, digested at 100° C. and filtered through dry papers; 5 grams of the filtrate were taken in each case and found to afford the results given in the table.

In 100 cc. $NH_4C_2H_3O_2$.	$PbSO_4$ dissolved in grams.			5°.
	Hot.	Cooled.	Cooled, 24 hours.	
28	0.356	....	....	3.47
30	0.418	....	0.226	3.12
32	0.494	0.451	0.242	2.73
35	0.513	0.452	....	2.89
37	0.529	....	0.238	2.90
40	0.539	....	0.263	3.27
45	0.555	0.488	....	3.34

In column 5° there is given, for each of the several degrees of dilution, the weight of ammonium acetate required to dissolve 1 gram of lead sulphate, from which it is seen that when in a solution of from 31 to 37 "volume per cent" (29 to 34.3 per cent) the ammonium acetate has the greatest solvent power.

In order, therefore, to dissolve lead sulphate, for each gram add 10 cc. of a 33 per cent. solution of ammonium acetate (sp. gr. = 1.07), heat to boiling, and filter promptly. In recovering the lead sulphate, it was found that the addition of 0.5 gram sulphuric acid greatly facilitated the evaporation and expulsion of the ammonium acetate, without loss.

UNIV. OF VA., June, 1898.

174. ANALYSIS OF SMITHSONITE FROM ARKANSAS.

BY W. W. MILLER, JR.

This mineral was received from the "Morning Star" Mine, in Searcy Co., on a branch of the White River, about 50 miles above Batesville, Ark. It occurs in a botryoidal form, enclosing zinc blende in layers 6 to 8 mm. thick, and encrusted by a thin layer of amorphous smithsonite. It is grayish-white in color, luster pearly, translucent, hardness = 5, sp. gr. = 4.179.

Upon analysis it afforded the following:

Zinc oxide	63.67
Cadmium oxide	1.06
Cupric oxide	0.21
Ferrous oxide	0.07
Carbon dioxide	34.69
Silica	0.52
	100.22

It proves, therefore, to be a pure variety of smithsonite, in which a little cadmium, copper, and iron replace zinc.

UNIV. OF VA., June, 1898.

DISULPHONES AND KETOSULPHONES.

BY ELMER P. KOHLER AND MARGARET B. MACDONALD.

The investigations of Otto and of Baumann have led to the discovery of excellent methods for the preparation of all classes of sulphones except disulphones and ketosulphones of the types represented by the formulas:

I. $\begin{matrix} RSO_2 \\ | \\ RSO_2 \end{matrix}$ II. $\begin{matrix} RCO \\ | \\ RSO_2 \end{matrix}$.

It seemed of particular interest to prepare members of the first class, because no substances are known that contain two hexavalent sulphur atoms in direct union. The marked tendency of sulphur to combine with sulphur, that is observed in the case of sulphides and other compounds containing bivalent sulphur, is absent in compounds containing hexavalent sulphur, and when sulphur compounds containing two sulphur atoms in direct union are oxidized, the union between the two is broken before both of them become hexavalent. These relations are illustrated by the following reactions:

I. $$2C_7H_7SH + O = \begin{matrix} C_7H_7S \\ | \\ C_7H_7S \end{matrix} + H_2O.$$

$$C_7H_7SO_2H + O = C_7H_7SO_3H.$$

II. $$2C_7H_7SNa + 2I = \begin{matrix} C_7H_7S \\ | \\ C_7H_7S \end{matrix} + 2NaI.$$

$$C_7H_7SO_2Na + I_2 = C_7H_7SO_2I + NaI.$$

By starting with disulphides, with two sulphur atoms in combination, it is possible to oxidize one to the hexavalent condition:

$$\begin{matrix} C_7H_7S \\ | \\ C_7H_7S \end{matrix} + 2O = \begin{matrix} C_7H_7S \\ | \\ C_7H_7SO_2 \end{matrix},$$

but further oxidation breaks the union between the sulphur atoms and leads to sulphonic acids:

$$\begin{matrix} C_7H_7S \\ | \\ C_7H_7SO_2 \end{matrix} + 3O + H_2O = 2C_7H_7SO_3H.$$

Some time ago Otto[1] tried to prepare disulphones of the type I, by using the reactions that are constantly employed for linking two residues through carbon, but without success. Thus benzenesulphone chloride and sodium give only sulphinate:

$$C_6H_5SO_2Cl + 2Na = C_6H_5SO_2Na + NaCl.$$

The sulphone iodides, which lose iodine with the greatest ease, give complicated reactions when heated with finely-divided silver:

$$3C_7H_7SO_2I + 3Ag = C_7H_7SO_2SC_7H_7 + \begin{matrix} C_7H_7SO_2 \\ \\ C_7H_7SO_2 \end{matrix}\!\!>O + 3AgI,$$

instead of the simple reaction expected:

$$2C_7H_7SO_2I + 2Ag = \begin{matrix} C_7H_7SO_2 \\ | \\ C_7H_7SO_2 \end{matrix} + 2AgI.$$

Because of these and similar reactions Otto[2] concluded that disulphones of type I were probably incapable of existence.

Some observations made in the course of an investigation of the reaction between metallic derivatives and sulphone chlorides led us to attempt the preparation of this class of substances in a different way. Among the reaction-products of perfectly pure aliphatic and aromatic sulphone chlorides with a variety of reagents, we have frequently observed a minute quantity of some sulphur compound, that, owing to

[1] Ber. d. chem. Ges., **24**, 478. [2] *Loc. cit.*, **24**, 484.

its insolubility in water, generally forms a scum on the surface of the liquid used. The insolubility of the substance, its stability on heating, and its inertness to reagents, pointed to some kind of sulphone, while the fact that the same substance or similar substances are obtained in a great variety of reactions indicated that only the sulphone chloride is involved in its formation. In the investigation above referred to we noticed that a substance of this kind was formed only in those experiments in which there was protracted heating and an insufficient amount of base. This suggested that the substance might be a disulphone formed by the interaction of a sulphone chloride and a sulphinate :

$$C_6H_5SO_2Cl + C_6H_5SO_2Na = NaCl + \begin{matrix} C_6H_5SO_2 \\ | \\ C_6H_5SO_2 \end{matrix}.$$

We have found that this reaction gives a simple and, apparently, a perfectly general method for the preparation of disulphones of this kind.

The reaction leaves but little doubt as to the structure of the substances obtained. If the sulphinate has the structure usually assigned to it and acts accordingly, the resulting substance must be a disulphone with the structure given. If, on the other hand, the sulphinate reacts in the desmotropic form :

I. $C_6H_5S(=O)ONa$,[1]

the product might be an anhydride with the structure

$$\begin{matrix} C_6H_5SO \\ >O. \\ C_6H_5SO_2 \end{matrix}$$

This formula, however, is not at all in accord with the extreme stability of the substance. It is not changed by prolonged boiling with dilute or concentrated hydrochloric acid, and it can be crystallized, without loss, from concentrated nitric acid.

The success with the sulphone chlorides naturally sug-

[1] Ber. d. chem. Ges., 18, 2493.

gested a similar experiment with other kinds of acid chlorides. We have found that the reaction works equally well for the preparation of ketosulphones:

$$C_7H_7SO_2Na + C_6H_5COCl = \begin{matrix} C_6H_5CO \\ | \\ C_7H_7SO_2 \end{matrix} + NaCl.$$

The ketosulphones are remarkably active substances, giving all the typical ketone reactions, but showing a much more reactive oxygen atom than that in other ketones.

The two classes of substances are now under investigation, hence this paper is confined to those results which are necessary to show the general character of the reactions and the structure of the products.

Diparatolyldisulphone, $(p)CH_3.C_6H_4.SO_2.SO_2.C_6H_4.CH_3(p)$. —Paratoluenesulphone chloride and sodium paratoluenesulphinate react slowly in water, ether, benzene, and acetone. As the result of a number of experiments we have adopted the following method of procedure: 1 molecule of the sulphinate is placed in a flask with sufficient water to form a thick paste; 1 molecule of sulphone chloride and a small quantity of ether are added to this, and the whole warmed in a water-bath until all of the sulphone chloride has disappeared; or until the solid that separates no longer increases in amount. The liquid is then filtered while hot. The aqueous solution contains sodium chloride, sodium sulphonate, and sulphinic acid. It is neutralized with sodium carbonate, returned to the flask with another molecule of sulphone chloride and a small quantity of ether, and heated as before. The finely-divided crystalline solid obtained in the two operations, is boiled with water to remove small quantities of adherent sulphinic acid, dried on the water-bath, extracted with small quantities of boiling ether to remove any sulphone chloride carried down with it, and recrystallized from large quantities of benzene. From the concentrated solution in boiling benzene the substance separates, on cooling, in small, lustrous plates that adhere to the sides of the vessel. From a cold benzene solution it separates, on evaporation, in thick, monoclinic tables that sometimes reach a diameter of 5 to 6 mm. An analysis of the

substance prepared in this way gave the following results:

I. 0.1551 gram substance gave 0.3073 gram CO_2, and 0.0597 gram H_2O.

II. 0.1609 gram substance gave 0.3196 gram CO_2, and 0.0621 gram H_2O.

III. 0.1273 gram substance gave 0.2041 gram $BaSO_4$.

IV. 0.1960 gram substance gave 0.2919 gram $BaSO_4$.

V. 0.1503 gram substance gave 0.2259 gram $BaSO_4$.

	Calculated for $C_7H_7SO_2$.	Found. I.	II.	III.	IV.	V.
C	54.19	53.9	54.1	....	....	....
H	4.51	4.26	4.3	....	....	....
S	20.64	...	...	20.49	20.45	20.64

A molecular weight determination by the cryoscopic method with naphthalene as the solvent gave the following results:

I. 1.63 grams substance per 100 grams of solvent gave a mean depression of 0.355°.

II. 2.53 grams substance per 100 grams of solvent gave a mean depression of 0.565°.

III. Constant for naphthalene 70.

	Calculated for $(C_7H_7SO_2)_2$.	Found. I.	II.
Molec. wt.	310.0	321.0	313.0

The substance is insoluble in water and alcohol, very slightly soluble in ether, moderately soluble in chloroform and boiling benzene. In a capillary tube it melts with decomposition at about 212°. The substance is remarkably inert. It is not attacked by dilute acids or alkalies. When boiled with concentrated potash, however, it is slowly decomposed. The solution contains a sulphinate and a sulphonate, which were identified as follows: The clear solution in caustic potash was acidified with hydrochloric acid and extracted with ether. The ether, on evaporation, deposited crystals of paratoluenesulphinic acid melting at 85°. The aqueous solution from which all the sulphinic acid had been extracted was neutralized, evaporated to dryness, and extracted with absolute alcohol. The alcoholic extract was evaporated to dryness and treated with phosphorus pentachloride. It gave paratoluene-

sulphone chloride melting at 69°. The decomposition with alkalies, therefore, takes place according to the equation:

$$C_{14}H_{14}S_2O_4 + 2KOH = C_7H_7SO_2K + C_7H_7SO_3K + H_2O.$$

This reaction excludes all possible formulas except the two given in the introduction:

I. $\begin{matrix} C_7H_7SO \\ C_7H_7SO_2 \end{matrix}>O$ and II. $\begin{matrix} C_7H_7SO_2 \\ | \\ C_7H_7SO_2 \end{matrix}$.

A substance with the anhydride formula represented by I. ought to be as easily hydrolyzed by acids as by alkalies, but the substance in question can be boiled with concentrated or dilute hydrochloric acid without any appreciable change. It is, therefore, diparatolyldisulphone.

Phenylparatolyldisulphone, $C_6H_5.SO_2.SO_2.C_6H_4CH_3(p)$.—This substance was prepared from benzenesulphone chloride and sodium paratoluenesulphinate, and also from paratoluenesulphonechloride and sodium benzenesulphinate:

$$C_7H_7.SO_2Na + C_6H_5.SO_2Cl = C_7H_7SO_2.SO_2C_6H_5 + NaCl;$$
$$C_7H_7.SO_2Cl + C_6H_5.SO_2Na = C_7H_7SO_2.SO_2C_6H_5 + NaCl.$$

It closely resembles diparatolylsulphone in crystal form and properties. It is moderately soluble in ether and benzene, readily soluble in chloroform, and melts at 166°. When heated with caustic potash it gives potassium chloride, potassium benzenesulphonate, potassium benzenesulphinate, potassium toluenesulphinate, and potassium toluenesulphonate.

Paratolylparanitroorthotolyldisulphone $(4)CH_3.C_6H_4.SO_2.SO_2.C_6H_3.CH_3.NO_2(2,4)$.—This substance crystallizes from chloroform in large, thick prisms, melting at 154°. It is noteworthy that when paranitroorthotoluenesulphone chloride and sodium paratoluenesulphinate react in the presence of water, some diparatolyldisulphone is always formed, indicating that some of the chloride reacts with the sulphinate according to the equation:

$$C_7H_6NO_2SO_2Cl + C_7H_7SO_2Na = C_7H_6.NO_2.SO_2.Na + C_7H_7.SO_2Cl.$$

We have observed a reaction like this when sulphuryl

chloride reacts with sulphinates in the presence of water:

$$C_7H_7SO_2Na + SO_2Cl_2 = C_7H_7SO_2Cl + NaSO_2Cl \longrightarrow NaCl + SO_2.$$

Phenylparatolylketosulphone, $\begin{matrix} C_6H_4CO \\ | \\ (p)CH_3C_6H_4SO_2 \end{matrix}$.—The sulphinates react with the chlorides of carbonic acids under the same conditions as those under which they react with sulphone chlorides. The best results are obtained by heating the sulphinates with ethereal solutions of the chlorides in sealed tubes.

Fifteen grams of benzoyl chloride, 20 grams of sodium paratoluenesulphinate, and 25 cc. of ether were heated to 110° for seventy-two hours. There was no pressure in the tube on opening. The contents were washed with water, and a solution of sodium carbonate added to remove sodium salts and unused benzoyl chloride. The aqueous solution contained sodium chloride, sodium sulphinate, and sodium benzoate, but no carbonate, sulphonate, nor sulphate. The ethereal solution was dried over anhydrous sodium sulphate, and the ether allowed to evaporate. There remained a clear, colorless oil, which could not be distilled without decomposition, and did not solidify on standing. This made it probable that the liquid obtained as a direct product of the reaction is the sulphoneketone expected, and that its solidification in contact with sodium carbonate is due to the addition of water. This was confirmed by the behavior of the liquid with water and alcohol. If it is digested with water on a water-bath for from ten to fifteen minutes, and then allowed to cool, it solidifies completely, the solid melting at 80°. If it is boiled with a small quantity of absolute alcohol for a short time, the corresponding crystalline alcoholate is obtained.

The substance is exceedingly stable; it does not lose water below 150°, and it is not possible to drive off all of the water without decomposing the substance. Both the oil and the solid readily react with the ordinary reagents for ketones, the oil being much more reactive than the solid. If the oil is shaken with a concentrated solution of hydrogen potassium sulphite it rapidly goes into solution, but in a short time a

beautiful crystalline addition-product begins to separate. The solid does not dissolve in hydrogen potassium sulphite. When allowed to stand in contact with a cold solution of sodium carbonate for several days the oil solidified to a white, crystalline mass. This was easily purified by recrystallization from low-boiling petroleum ether. It was thus obtained in thick needles melting at 80°.

I. 0.2755 gram substance gave 0.6130 gram CO_2, and 0.1480 gram H_2O.

II. 0.2077 gram substance gave 0.4608 gram CO_2, and 0.1007 gram H_2O.

III. 0.1655 gram substance (crystallized from ether) gave 0.3680 gram CO_2, and 0.0720 gram H_2O.

IV. 0.2112 gram substance gave 0.1786 gram $BaSO_4$.

V. 0.1705 gram substance gave 0.1429 gram $BaSO_4$.

	Calculated for $C_{14}H_{14}SO_4$.	Found. I.	II.	III.	IV.	V.
C	60.5	60.7	60.5	60.6	....	....
H	5.04	5.3	5.2	4.8	....	....
S	11.51	...	...	...	11.6	11.45

The analyses show that the substance is not the ketosulphone looked for, but an exceedingly stable hydrate analogous to chloral hydrate:

$$\begin{matrix} C_4H_5CO \\ | \\ C_7H_7SO_2 \end{matrix} + H_2O = \begin{matrix} C_4H_5C(OH)(OH) \\ | \\ C_7H_7SO_2 \end{matrix}.$$

It gives the same product if allowed to remain in contact with the solution for several days. Both oil and solid readily combine with nascent hydrocyanic acid, and give crystalline condensation-products with hydroxylamine, phenylhydrazine, primary amines, and phenols.

The reaction by which the substance was prepared seems to be a general one, as we have found that it works equally well with acetyl chloride, succinyl chloride, cinnamyl chloride, and phthalyl chloride. This has made it possible to prepare and study ketosulphones of which no carbon analogues are known. We hope to be able to report on some of these in the near future.

BRYN MAWR COLLEGE,
June, 1899.

THE REACTION BETWEEN SULPHONE CHLORIDES AND METALLIC DERIVATIVES OF KETONIC ESTERS.

By Elmer P. Kohler and Margaret B. MacDonald.

The reaction between acid chlorides and the metallic derivatives of ketonic esters and polyketones has been studied with great care, but the investigations have been confined to the chlorides of carbonic acids. In the cases studied the general result has been the replacement of one or more atoms of the metal by a corresponding number of acidyl groups. It is known, however, that the reaction between sulphone chlorides and metallic derivatives in general, is not nearly so uniform as that between other acid chlorides and the same substances. With alcoholates and phenolates the sulphone chlorides react like other acid chlorides, forming esters by double decomposition. With mercaptides a reaction similar to this takes place, but it is accompanied by a second one resulting in the formation of a sulphinate and a disulphide:

I. $C_7H_7SO_2Cl + NaSC_6H_{11} = C_7H_7SO_2SC_6H_{11} + NaCl$;[1]

II. $C_7H_7SO_2Cl + 2NaSC_6H_{11} = C_7H_7SO_2Na + (C_6H_{11}S)_2$.

With sulphides, thiophenolates, and zinc alkyls, only reactions of the second type have been observed:

I. $C_7H_7SO_2Cl + K_2S = C_7H_7SO_2K + KCl + S$;[2]

II. $C_7H_7SO_2Cl + 2NaSC_6H_5 = C_7H_7SO_2Na + (C_6H_5S)_2$;[3]

III. $2C_6H_5SO_2Cl + Zn(C_2H_5)_2 = (C_6H_5SO_2)_2Zn + 2C_2H_5Cl$.[4]

In nearly all of these cases the sulphone chlorides seem to behave differently from other acid chlorides. It is possible, however, that in these cases the sulphinates are secondary products, formed because the chloride was added to an excess of the other reagent.

The preliminary experiments with paratoluenesulphone chloride and sodium acetoacetic ester showed that it is impos-

1 Blomstrand: Ber. d. chem. Ges., **3**, 963.
2 Spring: Ber. d. chem. Ges., **7**, 1158.
3 Otto: *Ibid.*, **15**, 128.
4 Kalle: Ann. Chem. (Liebig), **119**, 156.

sible to get a complete reaction by using 1 molecule of the sodium derivative for 1 molecule of the sulphone chloride. If the relative amount of the former is increased until the mixture remains faintly alkaline after all of the sulphone chloride has disappeared, the main products are sodium chloride, sodium toluenesulphinate, and diacetosuccinic ester; but, in addition to these, acetoacetic ester, chloracetoacetic ester, and paratoluenesulphonacetoacetic ester are always formed. Similar experiments with sodium malonic ester and sodium acetylacetone gave analogous products. These substances, therefore, represent the normal products of the reaction between sulphone chlorides and the metallic derivatives of esters and ketones. All of them can easily be accounted for by assuming that the primary reaction is analogous to that which takes place between sulphone chlorides and zinc alkyls. In the case of acetoacetic ester this would lead to the following equations:

I. $C_7H_7SO_2Cl + CH_3COCHNaCO.OC_2H_5 = C_7H_7SO_2Na + CH_3COCHClCO.OC_2H_5$;

II. $CH_3COCHClCO.OC_2H_5 + CH_3COCHNaCO.OC_2H_5 = NaCl + \begin{matrix} CH_3COCHCO.OC_2H_5 \\ | \\ CH_3COCHCO.OC_2H_5 \end{matrix}$;

III. $CH\ COCHClCO.OC_2H_5 + C_7H_7SO_2Na = NaCl + \begin{matrix} CH_3CO \\ C_7H_7SO_2 \end{matrix}\!\!>\!CHCO.OC_2H_5$;

IV. $\begin{matrix} CH_3CO \\ C_7H_7SO_2 \end{matrix}\!\!>\!CHCO.OC_2H_5 + C_2H_5OH = C_7H_7SO_2CH_2CO.OC_2H_5 + CH_3CO.OC_2H_5$.

The third equation assumes the intermediate formation of a substance which was not isolated. All efforts to prepare this by the action of sodium sulphinate on chloracetoacetic ester failed; only the decomposition-products, ethyl acetate, and toluenesulphonacetic acid, were obtained. Attempts to condense acetoacetic ester and the sulphone chloride with potassium carbonate gave no better results, as the unused

carbonate decomposes the condensation-product as fast as formed.

The sodium derivative of the substance was, however, finally obtained in small quantity by a reaction that has not hitherto been used for the preparation of this class of substances. It has been found[1] that sodium acetoacetic ester reacts with sulphocyanates to form a mercaptide and sodium cyanacetoacetic ester. It seemed possible that by substituting an ester of a thiosulphonic acid a similar reaction might be obtained, resulting in the formation of a mercaptide and the sulphonacetoacetic ester. It was found that sodium acetoacetic ester readily reacts with the ester of paratoluenethiosulphonic acid, in the cold. The principal reaction is represented by the equation:

$$2CH_3COCHNaCO.OC_2H_5 + 2C_7H_7SO_2SC_2H_5 =$$
$$2C_7H_7SO_2Na + \begin{matrix} CH_3COCHCO.OC_2H_5 \\ | \\ CH_3COCHCO.OC_2H_5 \end{matrix} + (C_2H_5S)_2.$$

A subordinate reaction gives sodium toluenesulphonacetoacetic ester according to the equation,

$$C_7H_7SO_2SC_2H_5 + 2CH_3COCHNaCO.OC_2H_5 =$$
$$C_2H_5SNa + \begin{matrix} C_7H_7SO_2 \\ \diagdown \\ CH_3CO \end{matrix}\!\!>\!CNaCO.OC_2H_5 +$$
$$CH_3COCH_2CO.OC_2H_5.$$

The sodium derivative thus obtained is extremely unstable, breaking down into sodium sulphonacetic ester and acetic acid with the greatest ease. The free ester seems incapable of existence. A similar difference in stability was observed in the case of malonic ester. One of the products of the reaction between toluenesulphone chloride and disodium malonic ester was an ester salt of sodium toluenesulphonmalonic acid. This was sufficiently stable to permit of recrystallization from boiling alcohol, but on acidifying it immediately decomposed into carbon dioxide and toluenesulphonacetic ester:

$$C_7H_7SO_2CNa\begin{matrix} CO_2Na \\ \diagup \\ COOC_2H_5 \end{matrix} + 2HCl =$$
$$C_7H_7SO_2CH_2CO.OC_2H_5 + 2NaCl + CO_2.$$

[1] Kohler: This JOURNAL, **22**, 67.

Sodium Acetoacetic Ester and Paratoluenesulphone Chloride.

One gram-molecule of pure dry sodium acetoacetic ester and 1 gram-molecule of the sulphone chloride were brought together in absolute ether, and the mixture digested in a water-bath. After heating for an hour, a small portion of the mixture was removed and shaken with water. The aqueous solution was neutral to litmus, showing that all of the sodium derivative had disappeared, but the ether, on evaporation, left a considerable quantity of unchanged chloride. The heating was continued, small quantities of the sodium derivative being added from time to time, until the reaction remained faintly alkaline after all of the sulphone chloride had disappeared. One gram-molecule of the sulphone chloride required slightly more than 1.5 gram-molecules of the sodium derivative for complete reaction. The reaction-products were treated in various ways, in successive experiments, but as the substances obtained were always the same the following method of separation was adopted as the best: The contents of the flask were filtered, the insoluble sodium salts repeatedly extracted with ether, the ethereal solutions combined, and solution and solid treated separately.

The solid was boiled with absolute alcohol, which left only sodium chloride undissolved. The alcoholic solution, on cooling, deposited pure sodium toluenesulphinate. This was identified by analysis and by the melting-point of the acid obtained by acidifying the salt with hydrochloric acid.

I. 0.1674 gram substance gave 0.0654 gram Na_2SO_4.

II. 0.1829 gram substance gave 0.0721 gram Na_2SO_4.

	Calculated for $C_7H_7SO_2Na$.	Found. I.	Found. II.
Na	12.9	12.65	12.8

The melting-point of the acid was 85°.

The mother-liquor from the sodium sulphinate contained another sodium salt that was much more readily soluble in cold, absolute alcohol. This was purified by solution in cold alcohol and precipitation with ether.

I. 0.1480 gram substance gave 0.0407 gram Na_2SO_4.

II. 0.1759 gram substance gave 0.0430 gram Na_2SO_4.

	Calculated for $C_{11}H_{13}SO_4Na$.	Found. I.	Found. II.
Na	8.7	8.9	8.7

The substance is sodium paratoluenesulphonacetic ester. The aqueous solution was boiled with sodium carbonate and acidified, when it gave an acid melting at 118°. When this was boiled with alkalies it gave methyltolylsulphone melting at 88°. The product insoluble in ether contained no other organic substances. The amount of sodium chloride corresponded to 66 per cent of all the chlorine added, the sodium sulphinate represented 70 per cent, and the toluenesulphonacetic ester about 22 per cent of the sulphone chloride used.

The ethereal solution was acidified with dilute acetic acid, thoroughly washed with water, and dried with anhydrous sodium sulphate. After removing the ether, the residue was subjected to distillation under diminished pressure. It was thus separated into three portions: 1. A very low-boiling fraction composed of ethyl acetate, alcohol, and acetic acid; 2. A fraction that distilled over between 90° and 110° under a pressure of about 30 mm.; and 3. A fraction that could not be distilled without decomposition. The second fraction was changed into copper salts by the method of Wislicenus,[1] and the salts separated by recrystallization from carbon disulphide. Two salts were obtained, copper acetoacetic ester melting at 192°, and copper chloracetoacetic ester, identified by comparison with a specimen prepared from chloracetoacetic ester by the same method.

The third fraction solidified almost completely on standing. It was dried ~~on~~ a plate and repeatedly recrystallized from a mixture of ether and ligroin. It was thus separated into two substances, one of which was paratoluenesulphonacetic ester melting at 118°. The other substance melted at 69°, and gave the following results on analysis:

I. 0.2241 gram substance gave 0.4560 gram CO_2 and 0.1767 gram H_2O.

II. 0.2515 gram substance gave 0.5146 gram CO_2, and 0.1955 gram H_2O.

[1] Ber. d. chem. Ges., **31**, 3151.

	Calculated for $C_{13}H_{18}O_6$.	Found. I.	II.
C	55.81	55.5	55.8
H	6.97	7.1	7.0

The analysis, melting-point, and other properties showed that the substance is diacetosuccinic ester. That this is a secondary product due to the action of sodium acetoacetic ester on chloracetoacetic ester could be shown very clearly by varying the relative amounts of the reagents, and the time of heating. If the reaction was completed in a short time by using a considerable excess of sodium acetoacetic ester very little diacetosuccinic ester was obtained. With smaller quantities of sodium acetoacetic ester and more prolonged heating, on the other hand, very little chloracetoacetic ester remained, the principal products being the sulphinate and diacetosuccinic ester.

Sodium Malonic Ester and Paratoluenesulphone Chloride.

Since sodium malonic ester cannot be isolated in a pure condition, it was necessary to use malonic ester and sodium or malonic ester and sodium ethylate. In the earlier experiments malonic ester in benzene solution was treated with the calculated amount of metallic sodium, and the mixture allowed to stand until all of the sodium had disappeared.[1] A benzene solution of the sulphone chloride was then added, and the mixture heated on the water-bath until all the sulphone chloride had entered into reaction. It was found, however, that the protracted heating, required to complete the reaction in benzene solution, gave rise to so many secondary reactions that it was difficult to isolate pure substances from the products. It was found, also, that 1 molecule of sodium malonic ester is insufficient to react with 1 molecule of the sulphone chloride. Ether was, therefore, substituted for benzene, and sodium alcoholate for metallic sodium.

With 1 molecule of malonic ester, 1 molecule of the sulphone chloride, and sufficient sodium alcoholate to bring all of the sulphone chloride into reaction, the principal products are sodium chloride, sodium toluenesulphinate, and ethyl ethylenetetracarbonate.

[1] Conrad : Ann. Chem. (Liebig), **204**, 129.

Two and a half grams of sodium were dissolved in 6 grams of absolute alcohol and the mixture diluted with 150 cc. of ether; 20 grams of paratoluenesulphone chloride, dissolved in 200 cc. of ether, were added to this solution, and the whole boiled for three hours. Sodium alcoholate was then added in small portions, and the boiling continued until no sulphone chloride was left. The ether was removed by distillation, and the residue poured into water. The oil that separated was washed with water and dried on the water-bath. After standing for a few days it partially solidified in consequence of the separation of long, colorless needles. These, when purified by recrystallization from boiling water, melted at 79°. They were identified as ethyl ethylenetetracarbonate by comparison with a specimen prepared by treating chlormalonic ester with sodium malonic ester.

The oil from which the crystals had separated gave a good qualitative test for sulphur and chlorine. It could not be distilled in a vacuum, was not volatile with water-vapor, and gave no copper salts; hence its further separation was not attempted.

The aqueous solution was evaporated to dryness and extracted with absolute alcohol. The first crop of crystals from the alcoholic solution was sodium toluenesulphinate.

0.1522 gram of salt gave 0.0593 gram of Na_2SO_4.

	Calculated for $C_7H_7SO_2Na$.	Found.
Na	12.9	12.7

The filtrate from the sulphinate gave a considerable quantity of sodium tolueneacetic ester.

I. 0.1343 gram substance gave 0.0370 gram Na_2SO_4.

II. 0.1599 gram substance gave 0.0439 gram Na_2SO_4.

	Calculated for $C_{11}H_{13}SO_4Na$.	Found. I.	Found. II.
Na	8.7	8.86	8.88

It will be shown below that this substance is formed by the action of sodium toluenesulphinate on chlormalonic ester, the intermediate toluenesulphonmalonic ester being decomposed according to the equation:

$$C_7H_7SO_2CH\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix} + HOH =$$
$$C_7H_7SO_2CH_2CO.OC_2H_5 + C_2H_5OH + CO_2.$$

Paratoluenesulphone Chloride and Disodium Malonic Ester.

Two atoms of sodium were dissolved in the minimum amount of absolute alcohol and 1 molecule of malonic ester added to the well-cooled solution. The mixture was shaken until the sodium derivative began to separate, when 1 molecule of the sulphone chloride, dissolved in absolute alcohol, was added. The reaction was complete in twenty minutes. From the alcoholic solution ether precipitated a sodium salt, which after purification from alcohol gave the following results:

0.1547 gram substance gave 0.0662 gram Na_2SO_4.

	Calculated for $C_{11}H_{12}SO_4Na$.	Found.
Na	13.9	13.8

The composition of the substance corresponds to that of an ester salt of toluenesulphonmalonic acid. Its formation is explained by the observation of Bischoff,[1] that disodium malonic ester gives condensation-products derived from an ester salt of malonic acid:

$$C_7H_7SO_2Cl + 2CHNa\begin{matrix}CO_2Na\\COOC_2H_5\end{matrix} =$$
$$C_7H_7SO_2CNa\begin{matrix}CO_2Na\\COOC_2H_5\end{matrix} + CH_2\begin{matrix}CO_2Na\\COOC_2H_5\end{matrix} + NaCl.$$

The properties of the substance agree with the formula given. On acidifying its solution in water, carbon dioxide was given off and a substance, difficultly soluble in water, separated out. After purification this melted at 94° and gave the following analytical results:

I. 0.1434 gram substance gave 0.2864 gram CO_2, and 0.0642 gram H_2O.

II. 0.1180 gram substance gave 0.2351 gram CO_2, and 0.0516 gram H_2O.

[1] Ber. d. chem. Ges., 17, 2782.

	Calculated for $C_{11}H_{14}SO_4$.	Found. I.	II.
C	54.54	54.46	54.33
H	5.79	5.0	4.85

The substance is paratoluenesulphonacetic ester, formed according to the equation :

$$C_7H_7SO_2CNa\begin{matrix}CO_2Na\\COOC_2H_5\end{matrix} + 2HCl =$$
$$C_7H_7SO_2CH_2COOC_2H_5 + CO_2 + 2NaCl.$$

Sodium Toluenesulphinate and Chloracetoacetic Ester.

Some years ago Otto[1] studied the reaction between sodium benzenesulphinate and chloracetoacetic ester, and expressed the results by the equation :

$$CH_3COCHClCOOC_2H_5 + C_6H_5SO_2Na + H_2O =$$
$$C_6H_5SO_2CH_2COOC_2H_5 + CH_3COOH + NaCl,$$

assuming the intermediate formation of phenylsulphonacetoacetic ester. Otto's experiments do not show at what stage acetic acid is split off, hence they were repeated with paratoluenesulphone chloride using absolute alcohol, ether, or benzene as a medium. It was found that the substances do not react at all in absolute ether and benzene. In absolute alcohol they react very readily but the odor of ethyl acetate soon becomes perceptible, even if the mixture is allowed to stand in the cold. If the reaction is completed without warming, it takes place almost quantitatively according to the equation :

$$C_7H_7SO_2Na + CH_3COCHClCOOC_2H_5 + C_2H_5OH =$$
$$NaCl + CH_3COOC_2H_5 + C_7H_7SO_2CH_2COOC_2H_5.$$

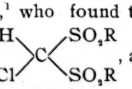
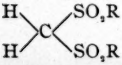
Eighteen grams of sodium toluenesulphinate were dissolved in 100 cc. of absolute alcohol and 17.5 grams of chloracetoacetic ester added. The mixture was allowed to stand in a tightly-corked flask for two weeks. The alcohol and ethyl acetate were then removed by drawing a rapid current of dry air through the liquid under greatly diminished pressure. The residue solidified completely, one recrystallization from ether gave

[1] Ber. d. chem. Ges., **23**, 756.

21.8 grams of pure paratoluenesulphonacetic ester instead of 24.2 grams calculated.

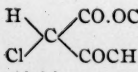
If the alcoholic solution of the substances is warmed on a water-bath, an entirely different reaction takes place; very little ethyl acetate and toluenesulphonacetic ester are obtained, most of the sulphinate being oxidized to sulphonate, and most of the chloracetoacetic ester reduced to acetoacetic ester.

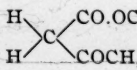
Seventeen and a half grams of chloracetoacetic ester were added to a solution of 18 grams of sodium toluenesulphinate in 50 cc. of boiling absolute alcohol. At first only sodium chloride separated, but after boiling for a few minutes the liquid became strongly acid and sodium toluenesulphonate began to crystallize out in characteristic plates. After boiling for about half an hour the alcohol was removed and the residue extracted with ether. The ethereal solution was washed with sodium carbonate, the ether removed by distillation, and the residue treated with copper sulphate and ammonia. It gave 11.8 grams of pure copper acetic ester, and a small quantity of copper chloracetoacetic ester. The sodium carbonate washings gave 4.5 grams of toluenesulphinic acid along with a trace of acetic acid.

The residue, insoluble in ether, was treated with absolute alcohol. It contained 15.8 grams of sodium toluenesulphonate. These results show that most of the sulphinate is oxidized at the expense of the chloracetoacetic ester. A similar reduction, in the case of chlorine substitution-products of disulphones, was observed by Fromm,[1] who found that when chlorinated disulphones of the type  , are treated with potassium hydroxide, 1 molecule is reduced to  , while another is decomposed, the sulphone groups being split off and oxidized to sulphonates or even sulphates.

In the experiments described above, the chlorketonic ester,

[1] Ber. d. chem. Ges., **31**, 185.



, is reduced to 

, by a sulphinate and alcohol.

The experiments were repeated with chlormalonic ester and chloracetylacetone with exactly similar results. In each case the course of the reaction depends upon the temperature and the concentration. In the cold and in dilute solution an acetyl or a carboxethyl group is replaced by the sulphone group; in boiling concentrated solution the sulphonate is oxidized, and the chlorester or ketone reduced. In boiling dilute solutions the two reactions take place at the same time.

Sodium Chloracetoacetic Ester and Sodium Toluenesulphinate.

The instability of substances like benzoylacetoacetic ester and benzoylacetylacetone is generally attributed to the accumulation of negative groups. Assuming this explanation to be correct, it seemed possible that the stability might be increased by the introduction of a positive metallic atom. This led to attempts to prepare a metallic derivative of paratoluenesulphonacetoacetic ester by starting with copper or sodium chloracetoacetic ester and the sulphinate. It was found that the copper compound could not be used, because it immediately reacted with the sodium sulphinate to form the sodium derivative of the chlorester and oxidation-products of the sulphinic acid. Sodium chloracetoacetic ester is much less reactive than the free ester, and can be used with advantage in the preparation of cyanacetoacetic ester and similar substances, but in the reaction under consideration it gives no better results. The only difference observed was that, in the case of the sodium derivative, there is very little oxidation of the sulphinate, the main products under all conditions being sodium chloride, sodium paratoluenesulphonacetic ester and ethyl acetate.

Sodium Acetoacetic Ester and Paratoluenethiosulphonic Ester.

A mixture of equivalent quantities of the substances in a large amount of absolute ether was warmed in a water-bath. At first only sodium sulphinate separated, but after heating for several hours a hard, granular deposit began to form on

the sides of the vessel. The heating was continued until this deposit no longer increased in amount—usually from thirty to forty hours. The ethereal solution was then poured off and the solids separated mechanically.

The ethereal solution contained only acetoacetic ester. The flocculent precipitate was dissolved in water, acidified with acetic acid, and distilled with steam. The distillate contained ethylmercaptan identified as the copper derivative. The residue, after distillation, was acidified with dilute sulphuric acid, when paratoluenesulphinic acid separated. The granular deposit was washed with ether, rapidly dried at 50°, and analyzed.

I. 0.1620 gram substance gave 0.0390 gram Na_2SO_4.

II. 0.2673 gram substance gave 0.0649 gram Na_2SO_4.

	Calculated for $C_{13}H_{18}SO_4Na$.	Found. I.	Found. II.
Na	7.52	7.8	7.9

The substance is so extremely unstable that it was impossible to free it from small quantities of mercaptide and sulphinate; but its properties show clearly that it is sodium toluenesulphonacetoacetic ester. It dissolves in water to form a neutral solution which almost immediately becomes acid. In a few minutes paratoluenesulphonacetic ester begins to crystallize out. If the aqueous solution is acidified with dilute sulphuric acid the separation is immediate and complete:

$$C_7H_7SO_2\diagdown\!\!\diagup CNaCO.OC_2H_5 + H_2O =$$
$$CH_3CO$$

$$C_7H_7SO_2CH_2COOC_2H_5 + CH_3CO_2Na.$$

One and a half grams of substance gave 1.05 grams of toluenesulphonacetic ester instead of 1.21 grams calculated.

When treated with cold absolute alcohol, the odor of ethyl acetate soon becomes perceptible, and the granular solid swells up in passing into the bulky sodium toluenesulphonacetic ester:

$$C_7H_7SO_2\diagdown\!\!\diagup CNaCO.OC_2H_5 + C_2H_5OH =$$
$$CH_3CO$$

$$C_7H_7SO_2CHNaCO.OC_2H_5 + CH_3COOC_2H_5.$$

With aqueous and alcoholic potash the substance gives tolylmethylsulphone, but not a trace of sulphinate or sulphonate, showing that the sulphinate obtained in the reaction between sulphone chlorides and metallic derivatives is a primary product. It will be observed that all the reactions of the substance are analogous to those of benzoylacetoacetic ester, the only difference between the two being the greater reactivity of the former.

The yield of the substance is always exceedingly small. The most favorable results were 2 grams of substance from 30 grams of sodium acetoacetic ester.

BRYN MAWR COLLEGE,
June, 1899.

NOTES.

The Boiling-point of Liquid Hydrogen as Determined by a Rhodium-platinum Resistance Thermometer.

In a recent number of the Proceedings of the Chemical Society there is an interesting note on the above subject by Professor Dewar which is here for the most part reprinted: Within the last week the author has succeeded in obtaining 250 cc. of colorless liquid hydrogen, and this has been employed in a redetermination of the boiling-point. Earlier observations made with a pure platinum resistance thermometer have given —238° as the boiling-point, and a new thermometer constructed from pure platinum from a different source gave practically the same result. As this might be affected by some constant error, the determination was checked by employing a thermometer constructed from an alloy of rhodium and platinum, containing 10 per cent of the former. Alloys had been shown by Professor Fleming and the author to differ from pure metals in showing no sign of becoming perfect conductors at the absolute zero of temperature, and a study of the rhodium-platinum alloy had shown that the change in conductivity produced by cooling from 0° to the boiling-point of liquid air is regular, and may be represented by a straight line. As determined by the rhodium-platinum thermometer the boiling-point of hydrogen was found to be —246°. Two ways of explaining the discrepancy between the two determinations suggested themselves. Pure platinum, although its resistance may be represented by a straight line almost down to the solidifying point of air shows signs of a departure from regularity at about this point, and

the curve may become asymptotic at lower temperatures. On the other hand, the resistance of the rhodium-platinum alloy diminishes less rapidly at these lower temperatures and is much higher than that of pure platinum under similar conditions. It follows that its resistance-temperature curve, in all probability, deviates less from a straight line than is the case with platinum. Either cause would explain the differences observed, but the lower boiling-point, —256°, or 27° absolute, seemed to be the more probable, as it agreed very fairly with the value for the boiling-point calculated by the author from Wroblewski's results and that arrived at by Olszewski. As the use of other pure metals could not lead to more satisfactory results, the problem must be attacked in a different way by means of an "air" thermometer containing hydrogen under diminished pressure.

Addendum.—Since this paper was communicated, the author has made a first attempt at determining the boiling-point by a constant volume hydrogen thermometer working under diminished pressure. The result is that this thermometer, which gave the boiling-point of oxygen as 90.5° absolute, or —182.5°, gave for hydrogen, 21° absolute, or —252°. The three determinations that have been made are then as follows: (1) Pure platinum resistance thermometer, 35° absolute; (2) rhodium-platinum resistance thermometer, 27° absolute; (3) hydrogen thermometer, 20° absolute. From this it appears that the boiling-point of hydrogen is really lower than was anticipated. The experiment will be repeated with thermometers fitted with hydrogen prepared from different sources. The boiling-point should be determined by the use of a hydrogen thermometer fitted with gas obtained from the evaporation of the liquid hydrogen itself.

On the Blue Color of Water.

In an article that appeared in No. 1, Vol. XVIII, of the Receuil des Travaux Chimiques des Pays-bas et de la Belgique, W. Spring again discusses the question as to the cause of the blue color of water. Many physicists have regarded the blue color of the sea and of lakes as not belonging to the water itself, but as being produced by the reflection of the sunlight from invisible particles which the water always contains in suspension. This idea was suggested by the theory then held regarding the cause of the blue color of the sky. Earlier experiments of Spring led him to the conclusion that water itself is blue, and that the fine particles which it holds in suspension, while contributing very much to its illumination, exert no appreciable influence on the intensity of the blue

color. Soret had previously, in 1869, expressed this same opinion. As neither the work of Soret nor that of Spring appears to have convinced every one, Spring has again taken up the subject with the object of determining experimentally the optical properties of the particles contained in clear waters. Parallel rays from a powerful electric light were passed through (1) distilled water, (2) the drinking water of Liège, and (3) rain water that had been allowed to stand. In all cases the presence of particles became apparent, the clearest being the drinking water. There was no evidence of a blue color. Now four experiments were performed :

1. A cell containing a solution of magenta was interposed between the source of light and the tube containing the water, so that only red light passed through the latter. Under these conditions the light appeared red and its intensity was not diminished.

2. The light was passed through a solution of picric acid before it was passed through the water. The yellow light was not in the least modified by being passed through the water.

3. The water was illuminated by blue light produced by interposing a cell containing an ammoniacal solution of cupric hydrate or a piece of cobalt glass. The result was the same as in the first two experiments. The color was not changed by passing the light through the water.

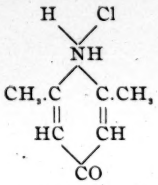
4. Green light produced by passing it through a solution of nickel chloride gave the same results, that is to say, the color was not changed.

These experiments show that the particles, to which clear water, distilled or natural, owes its illumination, have the power to reflect the red, the yellow, and the green waves, and that they cannot, therefore, be the cause of the blue color of water. Reflecting with equal facility waves of all lengths, they return the sunlight to us without chromatic change. The author concludes that water is blue of itself, and that the particles which it holds in suspension are the principal cause of its illumination. According to their nature, they determine also the modification of the color of the water, and produce greenish tones when they do not destroy all the natural color. I. R.

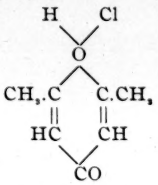
REPORT.

Quadrivalence of Oxygen.

In a recent paper[1] Collie and Tickle call attention to a number of reactions which can hardly be explained without assuming the quadrivalence of oxygen. In working with dimethylpyrone they obtained a substance, by the action of hydrochloric acid on it, which acted in a very peculiar manner. It behaved as an easily dissociated salt of a strong acid and weak base would behave, the dimethylpyrone being the basic substance. Further work showed that similar salts could be obtained with a number of acids. The easy breaking down into hydrochloric acid and dimethylpyrone when the salt is dissolved in water, and the decomposition of the other salts cannot be explained if the structure is as represented by the usual formula. If, however, these compounds are regarded as analogous to those formed by dimethylpyridone, the decompositions can be readily explained.



Dimethylpyridine hydrochloride.

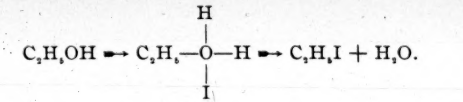


Dimethylpyrone hydrochloride.

The authors point out that this necessitates the assumption of the quadrivalence of oxygen, a view which is, however, supported by other evidence. Methylic ether hydrochloride, ethyl peroxide, and other compounds are considered by some to contain quadrivalent oxygen. Nef has called attention to similar cases in the peroxidized compounds studied by him, and Brühl has found that the results obtained in studying the refraction of hydrogen peroxide and water lead to the view that in these compounds the oxygen is quadrivalent. This has also served to explain the difference between such peroxides as MnO_2 and BaO_2, on the one hand, and CO_2 and SO_2 on the other. Oxygen also, as a typical element, might be expected to show a dual valency similar to its neighbors—nitrogen, sulphur, and phosphorus. We would expect this

[1] J. Chem. Soc., **75**, 710.

power to be weak and only shown in special cases. If oxygen is quadrivalent it may explain the great activity of oxygen compounds. This may be due to the residual unsatisfied affinity, and the action in the case of alcohol, for example, may take place thus:



Many reactions, as the oxidation and reduction of hydrogen peroxide, the formation either of *o*-, *m*-, or *p*-substituted compounds from oxygenated benzene compounds, and also etherification and hydrolysis, might be explained on such a basis. If oxygen can replace phosphorus, nitrogen, or sulphur in bases, these oxygen compounds can be regarded as derivatives of OH_2OH, as phosphorus compounds are derived from PH_3OH and nitrogen compounds from NH_4OH. J. E. G.

REVIEWS.

A Laboratory Outline of General Chemistry. By Alexander Smith, Chicago. Kent Chemical Laboratory of the University of Chicago. 1899.

The author begins his preface with these words: "No apology is offered for the preparation of another laboratory manual. Each teacher of chemistry sooner or later catches the infection, and finds himself impelled to prepare an outline of his own. There is little material that is original in the present one. The author therefore acknowledges his indebtedness to other similar outlines. Ramsay's 'Experimental Proofs of Chemical Theory' may be named as the source of some of the quantitative experiments."

Further on he says: "The work outlined is designed to occupy about six hours of laboratory work per week for nine months." The time required is the maximum that can well be required in a college course in chemistry, and there are probably but few colleges in the country where courses as full as this are given, or can well be given under existing conditions.

The course involves more quantitative work than usual, and there can be no doubt of the value of this kind of work. It takes time, especially if well done, and, if not well done, its value is much less; it may be even injurious. Some of the quantitative experiments described are no doubt capable of giving good results, while of others this cannot be said. One

would be inclined to think, for example, that the experiment on multiple proportions, p. 17, might easily miscarry when committed to the hands of the average college student. It may be, however, that all the experiments give excellent results when properly carried out. If so, Professor Smith has contributed something to the cause of laboratory teaching of chemistry.

The course is a "stiff" one, to use the technical adjective. It contains a good deal of detail, covering the field of general chemistry more thoroughly than most of those with which the writer of this notice is familiar.

One feature of the book will attract the attention of every reader, and that is the treatment of the subject of "ionization and interactions of acids, bases, and salts." It seems necessary, in view of the valuable results that have been reached through the study of solutions, that the theory of electrolytic dissociation should be brought to the attention of the student in the early stages of his work. The author recognizes this, and makes an effort to do his duty. Perhaps the work described in Chapter XI will leave a clear impression in the mind of the student, but it is difficult to see how it can, without a great deal of study—not mere reading of brief extracts from Ostwald and Walker.

On the whole, the book is clear and accurate and characterized by a strong infusion of common sense. I. R.

CHEMISTRY AND METALLURGY APPLIED TO DENTISTRY. By VERNON J. HALL, Ph.D., Professor of Chemistry and Director of the Chemical Laboratories in the Dental School and in the Woman's Medical School of Northwestern University. Evanston, Illinois: The Technical Press. 270 pp. $2.00.

In this book the author has confined himself strictly to the subjects having a bearing on dentistry. The non-metallic elements are not considered at all; but in Part I the general properties of the metals are briefly discussed, with the methods of analyzing mixtures and alloys. Part II contains a description of the general properties, methods of preparing, testing, and analyzing alloys, amalgams, amalgam-alloys, solders, dental cements, and gold, silver, and mercury. The author states in the preface that the student is expected to have received instruction in the elementary principles of chemistry before taking up this course; but it is hardly possible to give so much time to chemistry with the short time allowed for the entire course at most dental colleges. The amount of elementary chemistry taught in such a preliminary course varies in different institutions; but, unless some preliminary training in quantitative methods had been gained, the student would hardly be capable of obtaining the desired

results without considerable personal attention from the teacher. J. E. G.

VICTOR VON RICHTER'S ORGANIC CHEMISTRY, OR CHEMISTRY OF THE CARBON COMPOUNDS. Edited by PROF. R. ANSCHÜTZ, University of Bonn. Authorized translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American from the Eighth German Edition. Volume I. Chemistry of the Aliphatic Series. With illustrations. Philadelphia: P. Blakiston's Son & Co., 1012 Walnut St. 1899. pp. 626. Price, $3.00.

American chemists again have occasion to thank Professor Smith for preparing a translation of the latest German edition of Von Richter's well-known book, and also Professor Anschütz for his careful editing. As the translator says, "The student of the present edition will * * very quickly discover that the subject matter, so ably edited by Professor Anschütz, is vastly different from that given in the earlier editions. Indeed, the book has sustained very radical changes in many particulars, and certainly to its decided advantage. The book is, of course, characterized by true German thoroughness, while, at the same time, the treatment is systematic, and admirably adapted to the needs of the advanced student. The beginner would have a hard time of it were he to try to get an insight into the system of organic chemistry by the aid of this book, no matter how good a course of explanatory lectures might go with it. If, however, he has begun to see the principles of the system he could hardly find any better book to help him on.

The question of nomenclature is becoming a more and more pressing one in spite of the efforts of the Geneva Congress. The editor has made some use of the new names proposed by the congress, though he has not attempted to introduce and use them consistently. But who has? He says (p. 57): "The new names adopted by the Geneva Commission will, in the case of important series of compounds, be observed in the present text; they will be enclosed in brackets—*e. g.*, [ethene] for ethylene, [ethine] for acetylene, etc." Again, "The principles of this nomenclature have already encountered difficulties, especially in attempting to indicate in name a compound having a mixed character—*e. g.*, the body $COH—CH_2—CHOH—CO—CO_2H$, which would be *pentanolalon acid*.[1] The accumulation of suffixes, each of which possesses a meaning peculiar to itself, has 'conduit rapidement à des termes bizarres, d'une complication facheuse et d'une prononciation difficile' (Amé Pictet)."

Plainly, the only way to avoid the great and increasing difficulties encountered in the nomenclature of organic compounds is to stop making them, and annihilate many of those

[1] This would be *pentanolalonic acid*.—REV.

already made. This, according to a small body of chemists from whom we hear occasionally, would be a boon to chemistry. Of course, compound-making, however low an occupation it may be, is not going to stop. That it is going on in a very rapid way is evident to any one who will take the trouble to look into the subject. This book, covering only one-half of the subject—probably not that—will give the uninformed some idea of the extent of the field already cultivated. Fortunately there is nothing sad and depressing about this. It ought to be, and to many it is, inspiring. For it is only through the collection of material by every possible means that it will ever be possible to discover the possibilities of the chemical elements. Pernaps the most active compound-maker at present is Emil Fischer. Hofmann and Victor Meyer were great compound-makers. So is Von Baeyer, and so are many others of the leaders in chemistry. There are, too, compound-makers who do not contribute very valuable results. But that is the fault of the man, not of the occupation. It will hardly be claimed that all work in other fields of chemistry is necessarily good work.

But enough. Those who have felt called upon to express dissatisfaction with the fact that there is so much activity in field of organic chemistry are advised to give up a sufficient number of years to the study of the subject to justify them in expressing an opinion, and the book that has led to these somewhat inelevant remarks is highly recommended to them as a guide. I. R.

ELECTROLYSIS AND ELECTROSYNTHESIS OF ORGANIC COMPOUNDS. By DR. WALTHER LÖB, Privatdocent in the University of Bonn. Authorized translation from the author's enlarged and revised edition. By H. W. F. LORENZ, A.M., PH.D., graduate of the University of Berlin. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1898. pp. 103. Price, $1.00.

The study of the action of the electric current upon organic compounds is not new, as we owe important work in this field to Kekulé and to Kolbe, but it is only within a few years past that such work has been carried on with any activity. Results of value have been obtained, and the author of this book has undertaken to bring together the most important of these.

The book is made up of two parts, entitled, I. *Electrolysis and Electrosynthesis of Aliphatic Compounds*, and II. *Electrolysis and Electrosynthesis of Aromatic Compounds*.

Among the interesting processes described the following may be mentioned:

Iodoform is now manufactured by electrolysis of alcohol in a solution of an alkali iodide.

"If a galvanic current is conducted through acid or neutral aqueous solutions of aniline there is formed at the positive pole, besides other coloring-matters, aniline black, $C_{44}H_{31}N_4Cl$. Under similar conditions dyes are obtained at the positive pole from the salts of *toluidine*, *methylaniline*, *diphenylamine*, *ditolylamine*, and *phenyltolylamine*."

"*Naphthylamine salts* give naphthylamine violet. On electrolysis of *anthraquinone* and potassium hydroxide, Goppelsroeder succeeded in obtaining alivarin."

"According to a patent benzoyl-sulphone-imides can be prepared by the electrolytic oxidation of *toluenesulphone-amides*; for example, *o*-benzoyl-sulphone-imide, or saccharine, from *o-toluene-sulphone-amide*. I. R.

THE SPIRIT OF ORGANIC CHEMISTRY: An Introduction to the Current Literature of the Subject. By ARTHUR LACHMAN (B.S., PH.D.), Professor of Chemistry in the University of Oregon. With an introduction by PAUL C. FREER, M.D., PH.D., Professor of Chemistry in the University of Michigan. New York: The Macmillan Company; London: Macmillan & Co., L't'd. 1899. pp. 229. Price, $1.50.

The author informs us that "This book is intended primarily as a supplement to text-books of organic chemistry." He says, further, "A general principle of organic chemistry, therefore, must be examined by the side of definite experiments—an experiment is the very essence of definiteness. The present state of its development is best discerned by following its historic evolution by a study of its origin and of its career. A number of the chief problems of the science have been taken up in this manner and will be found to answer many of the questions that perplex the rising chemist. Problems which have had no history, which have been established in a single masterly research, manifestly do not fall within the scope of this collection." * * * "Secondly, students are not sufficiently encouraged to read the current literature; and its vastness proves an effective damper if no guide to its mazes be at hand. As most of the subjects selected here are still open questions, as the names of the investigators engaged upon them are prominently put forward, and as the journals in which these chemists are accustomed to publish their results are invariably quoted, no difficulty should be experienced in following up *these* topics at any rate."

The book is, in fact, made up of nine chapters, each of which deals with the development of some interesting and important subject. The titles of the chapters are: The Constitution of Rosaniline; Perkin's Reaction; The Constitution of Benzene; The Constitution of Acetoacetic Ether; The Uric Acid Group; The Constitution of the Sugars; The Isomerism of Maleïc and Fumaric Acids; The Isomerism of the

Oximes; The Constitution of the Diazo Compounds. It is perhaps enough to say that the author has shown clearly that he has grasped the significance of the problems he discusses, and that he undoubtedly has a very thorough knowledge of their literature. Further, he is himself much interested in the work, and, therefore, what he has to say is interesting. His language is in places picturesque, and not always conformable to the rules of grammar. Yet, taking the book as a whole, it can be warmly recommended to students who are trying earnestly to master the principles of organic chemistry.

A few extracts illustrating the author's style are here given: "At about this time (1869), Rosenstiehl found that different rosanilines were obtained according to whether ortho- or paratoluidine were employed for the purpose. These new facts did not collide with the then current theories, however, and Rosenstiehl made no effort to capitalize them. This was reserved for the future."

"The pivotal point, of course, was the recognition of triphenylmethane as the backbone of the group."

"A very limited number of facts had formed the basis of a brilliant and comprehensive generalization. The expectancy of the scientific world was roused to the highest pitch, and with feverish haste and activity all rushed to the chemical Eldorado to participate in its promised wealth of knowledge and insight."

"Kekulé made an attempt to determine the location of substituents by deduction from unfounded general principles."

"After these results the prism formula has not a leg left to stand upon."

"Baeyer studied the reduction products of benzene derivatives, with the idea in mind that the best way to get at the six valences was to put some of them out of the road."

"It supposes that the extra six valences do not directly unite but are attracted toward the center and neutralize each other all of a heap, so to speak."

"From this time on * * * the investigation was of an extremely desultory nature, consisting for the most part of theoretical disquisitions of a reprehensible character."

"At the same time Fischer's "hydrazine" standpoint seemed convincing and final."

"All of a sudden a bombshell was dropped into the diazo camp."

But, assuming this bombshell to have exploded,—though dropping a bombshell into a diazo camp is like carrying coals to Newcastle—the reviewer stops with the remark that any attempt to select all the gems from this book must fail as signally as an attempt to collect all the good things in David Harum.

I. R.